SOV/20-125-3-27/63

5(2,4)

AUTHORS: Rodionov, A. N., Vasil'yeva, V. N., Talalayeva, T. V., Shigorin, D. N., Gur'yanova, Ye. N., Kocheshkov, K. A., Corresponding Member, AS USSR

TITLE: Intermolecular Lithium Bond, Its Influence Upon the Vibration Spectra of Molecules and Upon the Dipole Moments (Mezhmolekulyarnaya litiyevaya svyaz', yeye vliyaniye na kolebatel'nyye spektry molekul i dipolnyye momenty)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 3, pp 562-565 (USSR)

ABSTRACT: In an earlier paper (Ref 1) the authors proved the formation of a bond referred to in the title $-\overset{-\delta}{CH_2}-\overset{+\delta}{Li}\ldots\overset{-\delta}{CH_2}-\overset{+\delta}{Li}$ (I) and R-O-Li...O-Li (II). The lithium bond like the hydrogen bond is a secondary chemical bond (Ref 2). Type (I) was closely investigated on the basis of infrared absorption spectra. In the work under review, infrared spectra of Alk-Li compounds with a varying length of the radical chain were solved in hexane and investigated at various concentrations. The aim was to clarify

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Intermolecular Lithium Bond, Its Influence Upon the Vibration Spectra of Molecules and Upon the Dipole Moments

the dependence of the intermolecular space, of the stability of the lithium bond and also of the magnitude of the frequency displacement of the groups C-Li on the length and on the structure of the carbon radical. Table 1 as well as figures 1 and 2 illustrate the results obtained. As may be observed therefrom, the value of the displacement of the said groups actually decreases with increasing chain length. Thus also the stability of the lithium bond in the complexes decreases. The investigation of the solutions of ethyl, n-butyl, and n-amyl lithium in hexane showed a linear course of the dependence of the dielectricity constant on the concentration in the case of lower concentrations. This course diverges from the straight line on an increase of concentration (0.4-3.0 mols %). The dipole moment of ethyl lithium in benzene remains constant between 0.08-0.43mols% and amounts to 0.87 D. The variation of the dipole moment in the complex, connected with the formation of lithium, goes back on the whole to the action of this bond upon the type of orientation of the dipoles with respect to one another. Therefore, the formation of cyclic complexes and especially the type

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Intermolecular Lithium Bond, Its Influence Upon the Vibration Spectra of Molecules and Upon the Dipole Moments

of the "quadrupoles" must decrease the dipole moment. This apparently takes place in the ethyl lithium solutions in benzene. It follows from the above that alkyl lithium molecules are associated both in benzene and in hexane solutions. The character of the associate depends both on the nature of the solvent and on the radical composition. The lithium bond considerably influences the frequency variations of the vibrations of the C-Li groups and also the dipole moments of the complexes; these variations here depend on the radical length, on the concentration of the solutions, and also on the nature of the solvent. There are 2 figures, 1 table, and 3 references, 2 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova (Scientific Physico-chemical Research Institute imeni L. Ya. Karpov)

SUBMITTED: December 29, 1958

Card 3/3

5 (2,3,4)

AUTHORS: Rodionov, A. N., Talalayeva, T. V., Shigorin, D. N., Kocheshkov, K. A., Corresponding Member AS USSR

SOV/20-128-4-26/65

TITLE: The Infrared Spectra and Structure of Aromatic Organolithium Compounds

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 4, pp 728 - 731 (USSR)

ABSTRACT: There are very few experimental data on the compounds mentioned in the title (Refs 1,2). To clarify the structure of these substances, the infrared absorption spectra of phenyl-, o- and p-tolyl-, mesityl-, p-diphenyl-, p-chlorophenyl-, p-bromophenyl-, p-iodophenyl-, as well as α- and β-naphthyl lithium were measured. These aromatic compounds are crystalline substances, and not soluble either in hexane or benzene. Therefore, the spectra of their powders were measured in vaseline- and fluorated oil. Table 1 shows that in these spectra several new bands appear which are in a certain connection with the C—Li bond. The data in table 1, as well as a comparison with spectra of aliphatic compounds previously described by the authors (Ref 5), lead to the conclusion that the band in the range of

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The Infrared Spectra and Structure of Aromatic Organolithium Compounds SOV/20-128-4-26/65

1045-1060 cm^{-1} is apparently connected with a free C-Li bond or, at least, with one poorly participating in the association. The lower frequencies (870, 970 cm^{-1}), however, may be related with the C-Li bonds participating in the association. These frequencies characteristic of the vibrations of the C-Li groups in the spectra of aromatic and aliphatic organolithium compounds, as well as their close position, speak much in favor of a covalent character of the said bond in the two classes of compounds mentioned. Therefore, the assumption of an ionic character of the C-Li bond in aromatic organolithium compounds found in publications is incorrect. The authors investigate the dependence on aromatic compounds responsible for the complex formation of aliphatic compounds of this type (formation of an intermolecular lithium bond and dipole interaction). In the present paper, they study not only the effect of the purely steric factor on the strength of the lithium bond but also that of the change in the general polarity of molecules. For this purpose, they introduce other polar groups or atoms into the organic rest of the molecule. On comparison of the spectra of phenyl-, o- and p-tolyl-, biphenyl- and mesityl lithium, it

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appears that the degree and type of association of these substances are different. The CH_3-group in orthoposition has little effect on the degree and character of association. The same group in paraposition (p-tolyl lithium), however, changes the spectrum considerably (Fig 1). A complication of the nonpolar substituent in paraposition equals an extension of the carbon rest. This reduces the degree of association. The screening effect becomes most distinct in the spectrum of mesityl lithium. The symmetrically arranged CH_3-groups render the association rather difficult. Therefore, only the band of the free C-Li group at about 1052 cm^{-1} is more or less distinctly visible. Figure 2 shows the spectra of p-chloro-, p-bromo-, and p-iodo-phenyl lithium. 2 dipoles each - C-Li and C-Hal - are present in every case. They increase the general polarity of the molecule. This brings about an intensification of the dipole interaction between the molecules. The p-chloro-phenyl lithium is most intensely and completely associated. The spectra of α- and β-naphthyl lithium are different from all other spectra dis-

The Infrared Spectra and Structure of Aromatic Organolithium Compounds SOV/20-128-4-26/65

cussed. The band is most intensive at 943 cm^{-1} while little intensive bands are present at 1050 cm^{-1}. In crystals, these two substances are apparently in a mainly associated state. There are 2 figures, 1 table, and 5 references, 3 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova (Scientific Physicochemical Research Institute imeni L. Ya. Karpov)

SUBMITTED: June 16, 1959

Card 4/4

SHI~~GORIN, D.~~ N,

66487

SOV/20-129-1-33/64

~~5(2,3,4)~~ 5.3700 (B)

AUTHORS: Rodionov, A. N., Kazennikova, G. V., Talalayeva, T. V., Shigorin, D. N., Kocheshkov, K. A., Corresponding Member AS USSR

TITLE: The Infra-red Spectra and Structure of Acetylenides of Lithium

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 1, pp 121-124 (USSR)

ABSTRACT: Acetylene and its derivatives can form complexes with each other and with several solvents by means of the hydrogen bond as well as interaction of π-electrons of the group: $-C \equiv C-$ (Ref 2). It could be assumed that the substitution of one hydrogen atom by one lithium atom in acetylene and acetylene derivatives with the aid of electrons of the C-Li bond and the π-electrons of the $C \equiv C$ group will increase the complex-forming capacity of these compounds. In order to explain the structure of this group of compounds the authors investigated the spectra of lithium compounds the authors investigated the spectra of lithium acetylenide, lithium methylacetylenide, lithium ethylacetylenide, lithium tertiary butylacetylenide, and lithium phenylacetylenide. Spectra of acetylenides and phenylacetylenides of potassium and sodium etc. were plotted in comparison. The results are summarized in figures 1 and 2 and table 1. The paper under review proved that

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the molecules of lithium acetylenides in crystals form stable complexes (ammonia) with each other as well as with other compounds. The recorded bands about 1060 and 1080 cm^{-1} may be assigned to the valence vibrations of the groups $\equiv C-Li$... in the complexes. The frequency of the valence vibration of the free groups $\equiv C-Li$ seems to be 1200 cm^{-1}, as was observed in the case of lithium phenylacetylenide. Thus the authors' assumption (Ref 6) that lithium acetylenides show a stronger tendency towards complex formation than acetylene itself has been proved. This may be explained by increased polarity of the $\equiv C-L$ bond (compared with $\equiv C-H$) as well as by a more probable cooperation of one valence electron of the lithium atom using the p-orbit. There are 2 figures, 1 table, and 6 references, 4 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova (Scientific Physico-chemical Research Institute imeni L. Ya. Karpov)

SUBMITTED: July 6, 1959

Card 2/2

SHIGORIN, D.N.

PHASE I BOOK EXPLOITATION SOV/4186

Akademiya nauk SSSR

Stroyeniye veshchestva i spektroskopiya (Structure of Matter and Spectroscopy) Moscow, Izd-vo AN SSSR, 1960. 113 p. Errata slip inserted. 2,300 copies printed.

Ed.: K. V. Astakhov, Professor; Tech. Ed.: T. P. Polenova.

PURPOSE: This collection of articles is intended for physicists and chemists interested in spectroscopic methods of research on the structure of molecules and related problems.

COVERAGE: The articles contained in this collection were taken from the editorial files of the Zhurnal fizicheskoy khimii (Journal of Physical Chemistry) and are concerned with spectroscopic methods in research on the structure of molecules, the hydrogen bond, isotopic effects, problems in magnetochemistry, the structure of aqueous solutions of electrolytes, and the chemistry of complex compounds. References accompany individual articles.

Pivovarov, V. M., and N. D. Ordyntseva. Features of Spectroscopic Manifestation of Hydrogen Bond in n-Nitroaniline Molecules 20

The authors thank Ya. S. Bobovich and V. S. Neporent for their interest.

Sheynker, Yu. N., and Ye. M. Peresleni [Khimiko-farmatsevticheskiy institut im. S. Ordzhonikidze (Chemical Pharmaceutical Institute imeni S. Ordzhonikidze)]. Tautomerism of Certain Derivative Heterocyclic Compounds. XI. The Deuteroeffect at Tautomeric Equilibrium and Spectra of N-Deutroacylated Heterocyclic Amines 28

Shigorin, D. N., M. M. Shemyakin, M. M. Kolosov, and T. S. Ryabchikova [Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physicochemical Institute imeni L. Ya. Karpov)] and Institut biologicheskoy i meditsinskoy khimii AMN SSSR [Institute of Biological and Medical Chemistry of the Academy of Medical Sciences USSR]. Intermolecular Interaction and Oscillation Spectra of Acetylene Compounds 36

Izmail'skiy, V. A., and V. Ye. Limanov [Moskovskiy pedagogicheskiy institut im. V. P. Potemkina-Moscow Pedagogical Institute im. V.P. Potemkin] Absorption Spectra of Derivatives of N-[β-(4-Nitrophenyl)-Ethyl]-Aniline 41

X Izmail'skiy, V. A., and V. Ye. Limanov [Moskovskiy pedagogicheskiy institut im. V. P. Potemkina (Moscow Pedagogical Institute imeni V. P. Potemkin)]. Absorption Spectra of Derivatives of N-[β-(2,4-Dinitrophenyl)-Ethyl]-Aniline 53

Rabinovich, I. B. [Gor'kovskiy gosudarstvennyy universitet im. N. I. Lobachevskiy (Gor'kiy State University imeni N. I. Lobachevskiy)]. Effect of Displacement of Hydrogen by Deuterium on the Molal Volume of Liquids 62

Card 3/6

10

S/048/60/024/006/019/030/XX
B013/B067

AUTHORS: Nurmukhametov, R. N., Shigorin, D. N., and Dokunikhin, N. S. ✓

TITLE: Luminescence of Solutions of Thioindigo and Its Two Derivatives at 77°K

PERIODICAL: Izvestiya Akademii nauk SSSR. Seriya fizicheskaya, 1960, Vol. 24, No. 6, pp. 728-729

TEXT: A method of producing luminescence spectra and a long-wave absorption line with a distinct structure (Ref. 1), developed by E. V. Shpol'skiy and his collaborators with aromatic hydrocarbons was extended by the authors to compounds with heteroatoms. Data are presented on the study of the spectra of thioindigo, 5.5'-dimethylthioindigo, and 6.6'-diethoxythioindigo which have a certain solubility in n-hydrocarbons. The solutions of these compounds frozen at 77°K yielded spectra with a distinct vibrational structure which, in the series of the solvents - from hexane to nonane - gradually became blurred. An absorption spectrum was obtained also for thioindigo in n-hexane. The relatively simple spectrum must be ascribed to the transition of the π-electron in the $>C=C<$ group.

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Luminescence of Solutions of Thioindigo
and Its Two Derivatives at 77°K

S/048/60/024/006/019/030/XX
B013/B067

Although the thioindigo molecule contains four heteroatoms, the long-wave absorption and emission spectra are caused by the $\pi \rightarrow \pi^*$-transition and not, as usual, by $n \rightarrow \pi^*$. The alcoholic solution which does not luminesce at all at room temperature, has a blurred emission spectrum at 77°K. Regarding its position, it is in agreement with the spectra of the n-hydrocarbon solutions. The similar behavior of alcoholic and neutral solutions indicates that the deactivation of molecules in alcohol is not only determined by H-bridges. A detailed description and analysis of spectra influenced by media with different intermolecular hydrogen bonds are given in Ref. 8. The present paper was read at the Eighth Conference on Luminescence (Molecular Luminescence and Luminescence Analysis) which took place in Minsk from October 19 to 24, 1959. There are 8 references: 4 Soviet, 1 German, and 1 US.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

Card 2/2

SHIGORIN, D.N.; SHCHEGLOVA, N.A.; DOKUNIKHIN, N.S.

Luminescence spectra of halide derivatives of anthraquinone in frozen solvents. Izv.AN SSSR 24 no.6:778-781 Je '60.
(MIRA 13:7)

1. Fiziko-khimicheskiy institut imeni L.Ya.Karpova.
(Anthraquinone--Spectra).

NURMUKHAMETOV, R.N.; SHIGORIN, D.N.; DOKUNIKHIN, N.S.

Luminescence of thioindingo solutions at low temperatures. Zhur. fiz.khim. 34 no.9:2055-2059 S '60. (MIRA 13:9)

1. Fiziko-khimicheskiy institut im. L.Ya. Karpova.
(Thioindigo)

67898

S/020/60/130/06/029/059
B004/B007

5.3700(A)

~~5(4)~~

AUTHORS: Piskunov, A. K., Shigorin, D. N.,
Smirnova, V. I., Stepanov, B. I.

TITLE: The Electron Paramagnetic Resonance Spectra of Some Chelate Compounds of Copper

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 130, Nr 6, pp 1284 - 1287 (USSR)

ABSTRACT: The authors investigated the e.p.r. spectra of the chelate compounds of copper with various azo-compounds as well as with the enol-form of acetylacetone and acetoacetic ester. Measurement of the magnetic moments showed that copper forms the compound with two valence electrons. If the initial state of the Cu-atom is d^9sp, it must have an unpaired electron. As, e.g., copper forms four equivalent bonds with acetylacetonate, it is presumed to enter into direct interaction with the π-electrons of the entire system. An investigation was carried out with the purpose of finding out whether the unpaired electron of the metal remains localized on the Cu-atom or whether it is delocalized in the molecule. Table 1 gives the experimental data of the compounds investigated: The width ΔH of the line

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67898

The Electron Paramagnetic Resonance Spectra of Some Chelate Compounds of Copper

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B004/B007

gicheskiy institut im. D. I. Mendeleyeva (Moscow Chemical-technological Institute imeni D. I. Mendeleyev)

PRESENTED: August 18, 1959 by V. A. Kargin, Academician

SUBMITTED: August 15, 1959

Card 3/3

81416

S/020/60/132/06/41/068
B004/B005

5.4130

AUTHORS: Shigorin, D. N., Shcheglova, N. A., Dokunikhin, N. S., Puchkov, V. A.

TITLE: The Nature of the Hydrogen Bond and Its Influence on the Electron Spectrum of Molecules

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 6, pp. 1372 - 1375

TEXT: In the introduction, the authors discuss data published on the influence of the hydrogen bond on the vibration spectra of molecules, mentioning papers by N. D. Sokolov (Ref. 1) and A. N. Frumkin (Ref. 5). Then, they investigate the coplanar system of α-hydroxy anthraquinone in which a π-electron interaction takes place, and the C=O group is decisive for the electron excitation. The authors assume the formation of a quasiaromatic ring by means of the H-bond (Fig. 1). The investigation of the electron vibration spectra of this compound and some of its derivatives yielded the valence vibration of the C=O group in the basic state. On absorption of a light quantum, a change in the distribution of

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The Nature of the Hydrogen Bond and Its Influence on the Electron Spectrum of Molecules

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B004/B005

the electron density, of the interatomic distances, etc. occurs which may lead to a solidification of the ring containing the H-bond (O-H....O=C). In the excited state, the action of the p-orbit of the H-atom becomes more probable. The rate of transformation of electron energy into vibration energy, and the probability of a redistribution of vibration energy on sublevels increase in this connection. The life of each excited vibration is reduced, and the luminescence spectra of the compounds containing the H-bond have a blurred fine structure. This is confirmed by the luminescence spectra of 1-hydroxy-, 1,4-, and 1-5-hydroxy anthraquinone which in fact show no fine structure (Fig. 2, insert after p. 1341). The luminescence spectra of α-methyl-, α-methoxy-, and α-phenyl anthraquinone (Fig. 2) having no H-bond show a fine structure. The data of the spectra are compiled in Table 1. The difference between absorption- and emission spectra is discussed; it is explained by the circumstance that the structure of the molecule and its electronic state change with the absorption of the energy quantum $h\nu_{abs}$; this change is only eliminated after emission of the light quantum $h\nu_{emiss}$. In substances with H-bond, the excited electron level formed after absorption of $h\nu_{abs}$ is not

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The Nature of the Hydrogen Bond and Its Influence on the Electron Spectrum of Molecules S/020/60/132/06/41/068 B004/B005

identical with the electron level at which emission begins (Fig. 3). Coplanarity is a condition for the occurrence of such intramolecular bonds. The increased interaction of a bridge with H-bond on the basis of 9-(p-hydroxy-)-phenyl acridine investigated by A. N. Terenin and V. V. Shablya (Ref. 13), and the important role of these phenomena in migration processes of the energy in high-molecular compounds (polyamides, protein, etc.) are pointed out. Levshin's law of mirror symmetry is mentioned. There are 2 figures, 1 table, and 15 references: 14 Soviet, 1 British, and 1 US.

X

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physical-chemical Institute imeni L. Ya. Karpov)

PRESENTED: February 11, 1960, by A. N. Terenin, Academician

SUBMITTED: February 14, 1960

Card 3/3

81733
S/020/60/133/01/49/070
B004/B007

5.3831
5.3100

AUTHORS: Shigorin, D. N., Rodionov, A. N., Talalayeva, T. V., Kocheshkov, K. A., Corresponding Member AS USSR

TITLE: An Investigation of the Nature of Secondary Chemical Bonds

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 133, No. 1, pp. 178 - 181

TEXT: The authors defined the formation of secondary (less strong) chemical bonds as an additional interaction of the valence electrons caused by a change in the energy-state of the electrons in the total system of chemical bonds of the molecule. The formation of secondary bonds thus does not depend solely on the nature of the atom entering into the molecule, but also on the properties of the molecular system and on the distribution of electron density in the molecule. The authors investigated the infrared spectra of lithium-organic compounds and acetylene derivatives. The infrared spectrum of R-Li and Ar-Li compounds shows a characteristic frequency of the valence oscillations of the free C-Li group at 1050 - 1100 cm^{-1}. Measurement of the dipole moments of R-Li

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An Investigation of the Nature of Secondary Chemical Bonds

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compounds in hexane gave the electric moment of 1.1 - 1.2 D for C-Li. The existence of oscillation frequencies and the low dipole moment indicate the covalence-character of the C-Li bond. In benzene- and hexane solutions of lithium-organic compounds as well as on their crystals, additional bonds were found, which lack in the vapor spectra, and which are due to complex formation. Like the compounds of Be, B, and Al, also the lithium-organic compounds form complexes by way of a secondary Li-bond. This is explained by means of the properties which these elements have in common: free energetically low p-orbits; the possibility of changing the energy state of the valence electrons in the direction s → p with only little energy. In this way, polycentric molecular electron orbits can be formed. These elements form chemical bonds not only by means of their valence electrons, but also by ceding free orbits to electrons which participate in the primary bond of other molecules. In the dimeric complex of lithium-organic compounds every C-atom of the carbon bridge with 2 Li-atoms is able to form a tricentral orbit (two electrons in the field of three nuclei). This orbit is more stable than the usual C-Li bond. For the initiation of the polymerization of ethylene and its derivatives under participation of R-Li or $Al(R)_3$, the formation of a complex[1] (I) is

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An Investigation of the Nature of Secondary Chemical Bonds

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assumed on the basis of these conceptions. Together with V. I. Smirnova, the authors proved the formation of radicals in the reaction of $TiCl_4$ with R-Li by means of electron paramagnetic resonance. The formation of complex (I) is proved by the colored complexes of ethyl lithium with styrene, α- and β-methyl styrene and other unsaturated compounds, which are characterized by an intense absorption band of the C=C bond. The authors discuss the formation of secondary bonds under participation of undivided electron pairs in the complexes R-Li...X (X = O<, N<, etc.) the σ,π-conjunction $\overset{+\delta}{Li}\overset{\sigma}{—}\overset{-\delta}{C}-C\overset{\pi}{=}C-$ in the compounds of benzyl lithium and fluorenyl lithium as well as the participation of the O-Li group, O-Al group etc. in secondary bonds in acetyl acetonates under formation of quasiaromatic rings with participation of π-electrons. Accordingly, there exist various types of secondary chemical bonds, which manifests itself in the physical properties and in the reactivity of the compounds. There are 13 references: 10 Soviet, 1 British, and 2 German.

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An Investigation of the Nature of Secondary Chemical Bonds

81733
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B004/B007

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: March 25, 1960

Card 4/4

SHIGORIN, D.N.; SHCHEGLOVA, N.A.; DOKUNIKHIN, N.S.

Luminescence spectra of halo derivatives of anthraquinone in frozen solutions. Dokl.AN SSSR 133 no.2:420-423 Jl '60. (MIRA 13:7)

1. Fiziko-khimicheskiy institut imeni L.Ya. Karpova. Predstavleno akademikom A.N. Terguinym.
(Anthraquinone--Spectra)

SHIGORIN, D.N.; POMERANTSEV, N.M.; SUMIN, L.V.

Characteristics of the proton magnetic resonance spectra of the α and β forms of polypeptide chains. Vysokom.soed. 3 no.4:560-561 Ap '61. (MIRA 14:4)

1. Fiziko-khimicheskiy institut imeni L.Ya.Karpova.
(Peptides) (Nuclear magnetic resonance and relaxation)

GASTILOVICH, Ye.A.; SHIGORIN, D.N.; GRACHEVA, Ye.P.; CHEKULAYEVA, I.A.;
SHOSTAKOVSKIY, M.F.

Investigating the nature of the complexes and derivatives of acetylene by the method of infrared absorption spectra. Opt.i spektr. 10 no.5:595-599 My '61. (MIRA 14:8)
(Acetylene--Spectra)

SHIGORIN, D.N.; KOZLOV, Yu.I.

Study of free radicals of the triphenylmethyl group with the aid of their luminescence spectra. Opt.i spektr. 10 no.5:600-606 My '61. (MIRA 14:8)

(Trityl group--Spectra)

NURMUKHAMETOV, R.N.; SHIGORIN, D.N.; KOZLOV, Yu.I.; PUCHKOV, V.A.

Effect of the hydrogen bond on the luminescence of hydroxy- and amino azo compounds. Opt. i spektr. 11 no.5:606-612 N '61. (MIRA 14:10)

(Azo compounds—Spectra)

NURMUKHAMETOV, R.N. (Moskva); SHIGORIN, D.N. (Moskva)

Nature of the luminescence spectra of anthraquinone and its β-derivatives in frozen solutions. Zhur. fiz. khim. 35 no.1: 72-79 Ja '61. (MIRA 14:2)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova.
(Anthraquinone—Spectra)

S/020/61/136/002/024/034
B016/B060

AUTHORS: Rodionov, A. N., Talalayeva, T. V., Shigorin, D. N., and Kocheshkov, K. A., Corresponding Member AS USSR

TITLE: Study of the Structure of Complexes of Organolithium Compounds With Ethers by Infrared Spectra

PERIODICAL: Doklady Akademii nauk SSSR, 1961, Vol. 136, No. 2, pp. 369-372

TEXT: The authors wanted to clarify the effect of ethers upon the structure and the character of complexes of organolithium compounds with the ethers. For this purpose they took infrared absorption spectra in the two-beam spectrometer type И-800 (N-800) featuring a NaCl prism. The following compounds were examined: methyl-, ethyl-, n-butyl, phenyl-, o-, m-, and p-tolyl, p-Cl- and p-Br-phenyl-, mesityl-, and fluorenyl lithium as well as the ethers: $(C_2H_5)_2O$, $(n\text{-}C_3H_7)_2O$, $(iso\text{-}C_3H_7)_2O$, $(n\text{-}C_4H_9)_2O$, and $(iso\text{-}C_5H_{11})_2O$. Table 1 gives the vibration frequencies

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Study of the Structure of Complexes of
Organolithium Compounds With Ethers by
Infrared Spectra

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B016/B060

(cm^{-1}) of the C-Li bond in fresh solutions of the mentioned organolithium compounds in the five ethers. Some of the former were synthesized directly in the respective ethers. The authors compared the spectra with the data obtained from their previous studies (Ref. 1) and in this manner assigned the absorption bands to the vibrations of the C-Li...O groups. The conclusion is drawn from an analysis of the data in Table 1 that almost all of the fresh solutions of the 11 substances mentioned display a similar spectrum in the same ether. The replacement of one ether by another has a remarkable effect upon the position of the C-Li...O group bands (Fig. 1 B). The analysis of the spectra proves that the more complicated the radicals used in the ethers, the farther the C-Li...O bands will be shifted in the region of shorter waves. It is inferred from results obtained that during the dissolution of organolithium compounds in ethers the primary complexes are deformed and decompose due to an acceptor-donor interaction and a dipole interaction with the ether. Subsequently, new complexes according to the acceptor-donor type

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Study of the Structure of Complexes of
Organolithium Compounds With Ethers by
Infrared Spectra

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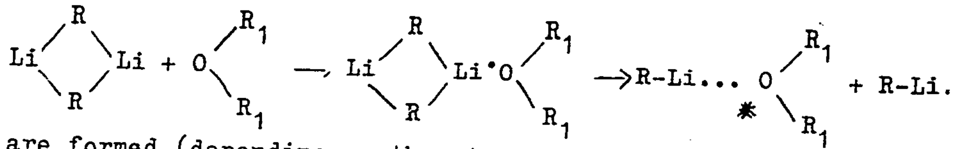
B016/B060



are formed (depending on the structure of the radicals of the two components) between the molecules of the ether and the organolithium compound. In this connection, the polarity of the C-Li bond is increased with increasing stability of the new complexes. In the authors' opinion, this is bound to express itself in a change both of the reactivity of the organolithium compound and its stability in the solution. This circumstance is believed to be the cause of the high activity of ethyl lithium in many reactions in the ethereal medium as well as of the poor stability of this substance in the same medium. There are 2 figures, 1 table, and 8 references: 4 Soviet, 3 German, and 1 British.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: September 14, 1960

Card 3/3

S/020/61/136/003/018/027
B016/B052

AUTHORS: Simonov, A. P., Shigorin, D. N., Talalayeva, T. V., and Kocheshkov, K. A., Corresponding Member AS USSR

TITLE: Examination of the Structure of Lithium Alcoholates by the Method of Infrared Absorption Spectra. O—Li...O Bond

PERIODICAL: Doklady Akademii nauk SSSR, 1961, Vol. 136, No. 3, pp. 634-637

TEXT: The authors examined the structure of R—O—Li bonds: tert.-C_4H_9OLi, CH_3OLi, C_2H_5OLi, n-C_3H_7OLi, and n-C_4H_9OLi. By measuring various properties of tert.-C_4H_9OLi (under the collaboration of V. N. Vasil'yeva, V. A. Dubovitskiy, and O. V. Nogina) the authors found that the O—Li bond of tert.-C_4H_9OLi is of a co-valent character, and the latter associates already in weak solutions. This was proven by infrared spectra in crystallized state and in solutions (Table 1). In hexane, CCl_4, cyclohexane, dioxan, di- and triethyl amine, these spectra hardly differed from those of the crystallized sample. Therefrom, and from the

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Examination of the Structure of Lithium
Alcoholates by the Method of Infrared
Abscrption Spectra. O—Li...O Bond

S/020/61/136/003/018/027
B016/B052

indifference of tert.-C_4H_9OLi toward active solvents and temperatures between + 70 and -80°C the authors conclude that its complexes are very constant. They attempted to explain the existence of such solid complexes as follows: 1. three-center intermolecular electron orbits are formed due to the fact that the Li atom of a molecule gives the free p-orbit to those electrons which take part in the O—Li σ-bond of another molecule. Consequently, one pair of valence electrons takes part in the formation of two O—Li...O bonds (see scheme Ia); 2. an acceptor - donor interaction sets in during which the unshared pair of p-electrons of the oxygen atom uses the free p-orbit of lithium in another molecule and thus additionally intensifies the intermolecular bond (I b). From the luminescence spectra of tert.-C_4H_9OLi (crystals and solutions in hexane), the authors conclude that either one electron changes over from the multi-center molecular orbit of the ground state into the excited multi-center orbit, or that the system is excited by the passage of one electron of the unshared pair of the oxygen atom into the multi-center orbit. The four other alcoholates studied, were spectroscopically examined in crystallized state (paste in

Card 2/3

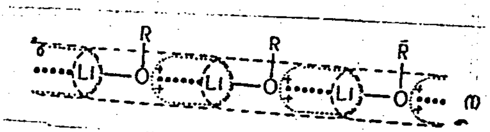
Examination of the Structure of Lithium Alcoholates by the Method of Infrared Absorption Spectra. O—Li...O Bond

S/020/61/136/003/018/027
B016/B052

vaseline or fluorinated oils) (Table 2). Since tert.-C_4H_9OLi is closely associated, the authors conclude that lithium alcoholates and unbranched aliphatic radicals are even more closely associated. This explains their insolubility or low solubility in solvents in which tert.-C_4H_9OLi is easily soluble. The authors approximately assigned the bonds of the four latter alcoholates to the complex oscillations of the associated O—Li groups. A more accurate assignment, however, will become possible by further investigations. There are 2 tables and 21 references: 4 Soviet, 1 US, 3 British, and 2 German.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: September 14, 1960



Card 3/3

PISKUNOV, A.K.; SHIGORIN, D.N.; STEPANOV, B.I.; KLINSHPONT, E.R.

Paramagnetic resonance of solutions of certain oxyazo copper compounds. Dokl. AN SSSR 136 no.4:871-874 F '61. (MIRA 14:1)

1. Fiziko-khimicheskiy institut imeni L.Ya. Karpova i Moskovskiy khimiko-tekhnologicheskiy institut imeni D.I. Mendeleyeva. Predstavleno akademikom V.A. Karginym.
(Copper compounds—Spectra)

23857
S/020/61/137/006/019/020
B101/B201

24,3500(1137,1138,1395)

AUTHORS: Shigorin, D. N., Shcheglova, N. A., and Dokunikhin, N. S.

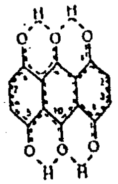
TITLE: Expressions of the autonomy of electron groupings in luminescence spectra of complicated molecules

PERIODICAL: Doklady Akademii nauk SSSR, v. 137, no. 6, 1961, 1416-1419

TEXT: A quantum-mechanical study of the electron levels of simple molecules
with multiple bonds has yielded the following results: 1) excitation is in
relation with the participation of π- and p-electrons of the chromogenic
group (>C=C<, C=O, etc.), on whose energetic state the substituents (auxo-
chromes) bear an influence. The authors of the present paper wanted to
clarify the problem as to whether the autonomy of electron groupings
(chromophores) appears both with absorption and with emission (luminescence).
The luminescence spectra of complicated molecules were examined, such as
anthraquinone (II), phenanthrene quinone (III), and anthrone (IV), as well
as thioindigo and its derivatives. The investigation was conducted at
concentrations of 10^{-4}-10^{-5} mole/l in n-paraffins, T = 77°K. Results are
presented in Fig. 1. For II, its α- and β-monohalogen-, α-methyl-, α-phenyl-,

Card 1/4

and α-methoxy derivatives, as well as for III and IV the following was found: the distance between the intensive bands and the weak bands amounts to 1664 cm^{-1} (for III and IV 1686 cm^{-1}) corresponding to the frequency of stretching vibrations of the chromophore C=O group. For mesobenzanthrone, its mono- and dibromo derivative, and for thioindigo the fine structure is, in accordance with E. V. Shpol'skiy (UFN, 68, 51 (1959); 71, 215 (1960)) characterized by the frequencies of the symmetric vibrations of condensed aromatic rings, and not by the frequencies of the stretching vibrations of the C=O group, which, consequently, does not act as chromophore in these compounds. It is inferred from the foregoing that an unequivocal autonomy of electron groups (chromophores) appears both in the absorption and luminescence spectrum of complicated molecules. These effects are best observed at low temperatures, since at higher temperatures the spectrum becomes unclear due to transformation of electron energy into vibrational energy of the rings. For molecules with two chromophore groups at low temperatures it has been noted that depending on the conditions of excitation (λ, temperature, medium) either electron state, but also both spectra, may be observed. A further fact that confirms the conservation and the strengthening of hydrogen bonds in α-hydroxy derivatives of anthraquinone in the excited state is the luminescence spectrum of 1, 4, 5, 8-tetrahydroxy anthraquinone. Each C=O group participates in two H bonds, so that four additional quasiaromatic rings, a quasi-corona



(X) forms.

The spectrum of this compound displays frequencies similar to those of the corona as well as frequencies that are characteristic of anthracene. A chromophore system is formed which comprises rings with H bonds, and in which the frequencies of the stretching vibrations of the C=O groups are no more determinative. The spectra of β-substituted anthraquinone (Br, I, R-C-C=O) allow the conclusion to be drawn that (under adequate conditions of excitation) the intensity of the Raman band of the chromophore (C=O) and the intensity, corresponding to the 0" - 0' transition in the luminescence spectrum, change. To conclude: local, "multicentered" electron orbits may arise with the participation of π electrons in complicated molecules. Academician

23857

S/020/61/137/006/019/020
B101/B201

Expressions of the ...

A. N. Terenin is thanked for discussions. There are 1 figure and 11 references: 10 Soviet-bloc and 1 non-Soviet-bloc. The reference to English-language publication reads as follows: E. Y. Bowen, B. Brocklehurst, J. Chem. Soc., 1954, 3875.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physicochemical Institute im. L. Ya. Karpov)

PRESENTED: November 9, 1960, by A. N. Terenin, Academician

SUBMITTED: November 2, 1960

Fig. 1. Luminescence spectra of anthraquinone derivatives in heptane at 77°K.
Legend: a) λ_{Hg} = 313 mμ; б) λ_{Hg} = 365 mμ; 1) α-chloroanthraquinone; 2) 1,8-dihydroxy anthraquinone; 3) 1,5-dihydroxy anthraquinone; 4) 1,4,5,8-tetrahydroxy anthraquinone (A = emission; 5 = absorption); 5) anthrone (in hexane), the shortwave part of the spectrum with λ_{init} = 4043 A is not shown;

Card 4/6

28676
S/020/61/140/002/021/023
B130/B110

5.4130

AUTHORS: Shigorin, D. N., Smirnova, V. I., Zhuravleva, G. S., Gracheva, Ye. P., and Shostakovskiy, M. F., Corresponding Member AS USSR

TITLE: Epr spectra of γ-irradiated acetylene and its derivatives

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 140, no. 2, 1961, 419-422

TEXT: To determine the relationship between the structure of the initial molecules and the structure of the resulting radical, the authors studied the epr spectra of γ-irradiated acetylene, methyl acetylene, methyl deutero acetylene, ethyl- and butyl acetylene, as well as phenyl- and methyl-phenyl acetylene at 77°K. The compounds were irradiated in special-glass ampuls giving no epr spectrum with the used dose of γ-radiation. Before the tests, the ampuls were evacuated to 10^{-3} mm Hg. Irradiation was conducted with Co^{60}. A superheterodyne radiospectroscope was used for taking the epr spectra. The magnetic field was calibrated with the epr spectra of the pyroxylamine disulfone ion, $[NO(SO_3)_2^{2-}]$ in

Card 1/3

28676

Epr spectra of γ-irradiated ...

S/020/61/140/002/021/023
B130/B110

during the experiments. There are 1 figure, 2 tables, and 4 references: 2 Soviet and 2 non-Soviet. The two references to English-language publications read as follows: C. P. Poole, S. Anderson, J. Chem. Phys., 31, no. 2, 346 (1959); R. West, Ch. Kreinzel, J. Am. Chem. Soc., 84, no. 4, 765 (1961).

X

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: May 25, 1961

Table 1. Integral intensity of γ-irradiation $\sim 10^7$ rad. Legend: (a) initial compounds (boiling point, ^oC), (b) radical presumed, (c) number of lines, (d) total width, oersteds, (e) the number of lines due to superposition with the spectrum of $CH_3-C\equiv C-H$ cannot be determined.

Card 3/5

SIMONOV, A.P.; SHIGORIN, D.N.; TALALAYEVA, T.V.; KOCHESHKOV, K.A.

Infrared absorption spectra of some R - O - Li compounds. (MIRA 14:11)
Dokl. AN SSSR 141 no.3:665-667 N '61.

1. Fiziko khimicheskiy institut im. L.Ya. Karpova. 2. Chlen-korrespondent AN SSSR (for Kocheshkov).
(Lithium organic compounds—Spectra)

SIMONOV, A.P.; SHIGORIN, D.N.; TALALAYEVA, T.V.; KOCHESHKOV, K.A.

Association of tert.C_4H_9OLi in the gaseous state. Izv.AN SSSR.-Otd.khim.nauk no.6:1126 '62. (MIRA 15:8)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova.
(Lithium butoxide--Spectra)

SHIGORIN, D.N.; VOLKOVA, N.V.; PISKUNOV, A.K.; GUREVICH, A.I.

Studying the triplet states of molecules by the methods of luminescence and electron paramagnetic resonance. Opt.i spektr. 12 no.5:657-659 My '62. (MIRA 15:5)

(Molecular dynamics) (Luminescence)

(Paramagnetic resonance and relaxation)

SHIGORIN, D.N.; NURMUKHAMETOV, R.N.; KOZLOV, Yu.I.

Luminescence of indigo solutions at 77°K. Opt.i spektr. 12 no.5:659-661 My '62. (MIRA 15:5)
(Indigo) (Luminescence)

YERMOLAYEV, V.L.; SVESHNIKOVA, Ye.B.; SHIGORIN, D.N.

Nonradiative energy transfer between the triplet and singlet states in organic molecules; discussion of A.N.Terenin and V.L. Ermolaev's report "Inactivation of the triplet state in aromatic molecules". Izv. AN SSSR. Ser. fiz. 26 no.1:29-31 Ja '62. (MIRA 15:2)

(Organic compounds)
(Molecular dynamics)

SIMONOV, A.P.; SHIGORIN, D.N.; TALALAYEVA, T.V.; KOCHESHKOV, K.A.

Study of the lithium alcoholate structure by the method of infrared absorption spectra; O-Li...O bond. Izv. AN SSSR.Ser.fiz. 26 no.10: 1246-1249 0 '62. (MIRA 15:10)

(Lithium alcoholate—Spectra)

SHCHEGLOVA, N.A.; SHIGORIN, D.N.; DOKUNIKHIN, N.S.

Luminescence of monohalo derivatives of anthraquinone in frozen solutions. Zhur. fiz. khim. 36 no.9:1938-1946 S '62.
(MIRA 17:6)

1. Fiziko-khimicheskiy institut imeni L.Ya. Karpova, Moskva.

RODIONOV, A.N.; SHIGORIN, D.N.; TALALAYEVA, T.V.; KOCHESHKOV, K.A.

Structure of complexes formed by aliphatic organolithium compounds. Dokl. AN SSSR 143 no.1:137-139 Mr '62. (MIRA 15:2)

1. Chlen-korrespondent AN SSSR (for Kocheshkov).
(Lithium organic compounds)

LOKSHIN, B.V.; PISKUNOV, A.K.; KAZITSYNA, L.A.; SHIGORIN, D.N.

Investigation of the structure of certain inner-complex compounds by means of electron paramagnetic resonance. Dokl. AN SSSR 143 no.4:867-870 Ap '62. (MIRA 15:3)

1. Moskovskiy gosudarstvennyy universitet im. M.V.Lomonosova. Predstavleno akademikom A.N.Nesmeyanovym.
(Complex compounds—Spectra)

NURMUKHAMETOV, R.N.; KOZLOV, Yu.I.; SHIGORIN, D.N.; PUCHKOV, V.A.

Luminescence spectra of azomethine compounds. Dokl. AN SSSR 143 no.5:1145-1148 Ap '62. (MIRA 15:4)

1. Predstavleno akademikom A.N.Tereninym.
(Schiff bases--Spectra)

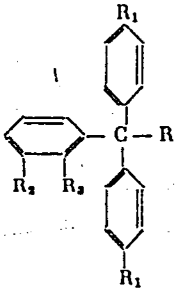
S/048/63/027/001/007/043
B163/B180

AUTHORS: Kozlov, Yu. I., and Shigorin, D. N.

TITLE: Formation of free radicals of the triphenylmethyl series

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Seriya fizicheskaya, v. 27, no. 1, 1963, 14-16

TEXT: Compounds of the following type



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S/048/63/027/001/007/043
B163/B180

Formation of free radicals of the ...

were studied, where R = H, OH, Cl, H_3C; R_1 = H, $N(CH_3)_2$, $N(C_2H_5)_2$, R_2 = H, Cl, OCH_3, NO_2; R_3 = H, OCH_3. In such compounds, the $\equiv C - R$ bond breaks under ultraviolet irradiation with wavelengths between 250 and 350 mμ. The formation of the radicals is proved by the epr in the irradiated compounds, and by the fact that the luminescence spectra of the particles obtained after irradiation of $(C_6H_5)_3CH$, $(C_6H_5)_3CCl$, $(C_6H_5)_3COH$ coincide with the spectrum of the free triphenylmethyl radical obtained by thermal dissociation of $(C_6H_5)CC(C_6H_5)_3$. Before irradiation, the molecules show strong fluorescence at 3800 - 4500 Å, and phosphorescence at 4200 - 4800 Å. Both fade as the irradiation time increases and the intensity of a new fluorescence band at about 5800 Å increases, which is specific for the resulting radicals. The phosphorescence of the initial molecules and the formation of radicals becomes stronger if the solvent is changed from benzene to hydrocarbons and alcohols. Since the energy of radical formation exceeds the energy of the exciting quanta (λ = 313 nm), a direct process is impossible, and

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Formation of free radicals of the ...

S/048/63/027/001/007/043
B163/B180

the following mechanism is suggested. First there is excitation of the π-electron system (singlet $\pi \rightarrow \pi^*$ transition) in the initial molecules. From this excited state a nonradiative transition to a triplet state with a lifetime of a few seconds is possible. Some of the molecules in the triplet state emit their energy in form of phosphorescence quanta, others transmit it to the system of σ-bonds $\geq C - R$ which is weakened and can now be broken up by ultraviolet radiation to form free radicals. The probability of formation of free radicals is lower for gamma-irradiation than for ultraviolet. This paper was presented at the 14th Conference on Spectroscopy in Gor'kiy, July 5-12, 1961. There are 2 figures.

Card 3/3

S/048/63/027/001/025/043
B108/B186

AUTHORS: Lokshin, B. V., Piskunov, A. K., Kazitsyna, L. A., and Shigorin, D. N.

TITLE: Investigation of the structure of some chelate compounds by means of electron paramagnetic resonance

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Seriya fizicheskaya, v. 27, no. 1, 1963, 75-77

TEXT: The e.p.r. spectra of several copper complexes formed by the alkyl- and aryl imines of saliçyl aldehyde, o-oxy acetophenone, and β-oxy naphthaldehyde in the form of powders and solutions in chloroform were studied. The powder samples displayed one single asymmetric absorption band and the solutions showed a hyperfine structure (three lines). This splitting is due to the interaction of the unpaired 3d electron of copper with the nucleus of the copper atom (nuclear spin 3/2). An additional hyperfine splitting into five lines was observed in the case of copper o-oxy acetophenone iminate, which is due to interaction of the unpaired electron with two equivalent nitrogen atoms (J = 1). This could

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Investigation of the structure ... S/048/63/027/001/025/043
B108/B186

not be resolved with the other compounds, but was also inferred from the dependence of the distance between the split lines on the structure of the groups around the Cu atom (ligand). The width of the e.p.r. lines of the solid compounds depends on the exchange interactions between the paramagnetic particles in the crystal. As the substituent increases, the volume of the molecule and their steric hindrance of close packing also increase. This leads to a reduced volume interaction and, in the case of equivalent packing of the paramagnetic particles in the crystal, to a narrowing of the e.p.r. lines. There are 2 figures and 1 table.

ASSOCIATION: Khimicheskiy fakul'tet Moskovskogo gos. universiteta im. M. V. Lomonosova (Chemical Branch of Moscow State University imeni M. V. Lomonosov)

Card 2/2

44946

S/048/63/027/001/026/043
B108/B186

5 1150

AUTHORS: Smirnova, V. I., Shigorin, D. N., and Zhuravleva, T. S.

TITLE: E.p.r. spectra of gamma-irradiated compounds with multiple bonds

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Seriya fizicheskaya, v. 27, no. 1, 1963, 78-80

TEXT: To establish a relationship between the structure of a molecule and that of its radical, the e.p.r. spectra of gamma-irradiated acetylenes and of compounds containing heterocyclic atoms were studied at 77°K. The method used is described in a previous paper (Dokl. AN SSSR, 140, no. 2, 419 (1961)). The results on the acetylenes are shown in Table 1. The large number of hyperfine lines is explained by the interaction of the unpaired electron with several protons of the system. Substitution of the CH_2 or CH groups by electronegative atoms in compounds containing O or N atoms changes the e.p.r. spectra of the radicals. The formation of radicals is associated with the breaking of the C-H bond of the methyl or methylene groups of the initial compounds.

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E.p.r. spectra of gamma-irradiated ... S/048/63/027/001/026/043
B108/B186

There are 2 figures and 2 tables.

Table 1. Legend: Integral power of irradiation ~10^7 rad. $t_{КИП}$ = boiling point (in °C). * width determined from the first derivative of the absorption curve. ** number of lines hard to determine because of superposition of the spectrum of not completely deuterized methyl acetylene, *** spectrum was not found even at a dose of $1-40 \cdot 10^6$ rad, **** e.p.r. spectrum obtained at a dose of $1.5 \cdot 10^7$ rad. (1) initial compounds, (2) assumed radical, (3) number of lines, (4) overall width of spectrum, oe.

Table 2. Legend: Integral power of irradiation ~$1.6 \cdot 10^7$ rad. * width determined from the first derivative of the absorption curve. ** data of the present authors. (1) initial compound, (2) assumed radical, (3) number of lines, (4) overall width of spectrum, oe.

Card 2/4

E.p.r. spectra of gamma-irradiated ...

S/048/63/027/001/026/043
B108/B186

Исходные соединения 1	Предполагаемый радикал 2	Число линий 3	Общая ширина спектра, Ое* 4
$H_3C-C\equiv C-H$ ($t_{кип}$ = −23,3°C)	$\lvert H_2C=C=CH\rvert^\bullet$	4	50,2 ± 1,4
$H_3C-C\equiv C-D$	$\lvert H_2C=C\equiv CD\rvert^\bullet$	**	97,5 ± 1,4
$C_2H_5-C\equiv C-H$ ($t_{кип}$ = 8,5°)	$\lvert H_3C-CH=C\equiv CH\rvert^\bullet$ $\lvert H_2C=C\equiv CH\rvert^\bullet$	*	
$C_4H_9-C\equiv C-H$ ($t_{кип}$ = 70,0°)	$\rvert CH_2-CH_2-CH_2-CH=C\equiv CH\rvert^\bullet$ $\lvert H_2C=C\equiv CH\rvert^\bullet \dot{C}_2H_5$	6(8) 11	54,8 ± 1,6 104,4 ± 2,4
$C_6H_5-C\equiv C-H$***	—	—	—
$C_6H_5-C\equiv C-CH_3$ ($t_{кип}$ = 71–72°)	$C_6H_5-C\equiv C-\dot{C}H_2$	3	34 ± 1,1
$HC\equiv CH$ **** ($t_{кип}$ = −83,6°)	$-\dot{C}=CH-CH=CH-CH=CH-$ $\dot{C}\equiv C-H$ $H-C\equiv C-H$ $H-C\equiv C-H$	10(12)	112 ± 4

Table 1

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E.p.r. spectra of gamma-irradiated ...

S/048/63/027/001/026/043
B108/B186

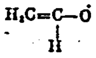
Исходные соединения 1	Предполагаемый радикал 2	Число линий 3	Общая ширина* спектра, Ое 4
$H-CH=O$	—	4	$36 \pm 1,0$
$CH_3-CH=O$	 $H_2C=\underset{H}{\underset{\mid}{C}}-\dot{O}$	6(8)	$86 \pm 2,0$
$CH_2-CH=CH_2$	$\lvert H_2C\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2\rvert$	5	$58 \pm 1,5$**
$CH_3-C\equiv N$	$\lvert H_2C\overset{\cdots}{-}C\underset{\cdots}{\equiv}N\rvert^{\cdot}$	9	$\sim 55,0$
$C_2H_5-C\equiv N$	$\lvert H_3C-CH\overset{\cdots}{-}C\underset{\cdots}{\equiv}N\rvert^{\cdot}$	13(15)	$\sim 64,0$

Table 2

Card 4/4

ACCESSION NR: AT4033990 S/0000/63/000/000/0081/0086

AUTHOR: Rodionov, A. N.; Asnovich, E. Z.; Shigorin, D. N.; Andrianov, K. A.

TITLE: Infrared absorption spectra of some metallic silicones

SOURCE: Geterotsepny*ye vy*sokomolekulyarny*ye soyedineniya (Heterochain macromolecular compounds); sbornik statey. Moscow, Izd-vo "Nauka," 1963, 81-86

TOPIC TAGS: polymer, silicone, siloxane, polyorganosiloxane, metallic silicone, aluminum containing silicone, titanium containing silicone, tin containing silicone, silicone spectral analysis, polyphenyl siloxane, polymethyl siloxane, polyethyl siloxane

ABSTRACT: Absorption spectra of polymethyl-, polyethyl- or polyphenyl siloxanes containing Al, Ti or Sn in various ratios to Si were analyzed for the range 400-1100 cm^{-1}. Bands corresponding to Si-O valence fluctuation in the Si-O-Sn group were identified at 900-980 cm^{-1}, those for Sn-O at 530-580 cm^{-1}. Band intensities in these spectral regions varied for all polymers in relation to the metal/Si ratio, indicating preservation of absorption frequencies of the Si-O-metal group during monomer to polymer conversion. Location of absorption bands for such group varied little from one metal to another. Orig. art. has: 3 graphs, 2 tables.

Card 1/2

ACCESSION NR: AT4033990

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Institute of Physical Chemistry); Institut elementoorganicheskikh soyedineniy AN SSSR (Institute of Metalloorganic Compounds AN SSSR)

SUBMITTED: 06Jul62 DATE ACQ: 30Apr64 ENCL: 00

SUB CODE: OC NO REF SOV: 004 OTHER: 003

Card 2/2

KOZLOV, Yu. I.; SHIGORIN, D. N.

On the formation of free radicals of the triphenylmethyl series. Izv. AN SSSR. Ser. fiz. 27 no.1:14-16 Ja '63. (MIRA 16:1)

(Trityl group) (Radicals(Chemistry))

15Oct

L 14959-63 EPR/EWP(j)/EPF(c)/EWT(1)/EWT(m)/BDS/EEC(b)-2 AFFTC/ASD
Ps-4/Pc-4/Pr-4/Pi-4 GG/RM/WW

85

ACCESSION NR: AP3000315 S/0048/63/027/005/0634/0637 81

AUTHOR: Piskunov, A. K.; Nurmukhametov, R. N.; Shigorin, D. N.; Muromtsev, V. I.; Ozerova, G. A.

TITLE: Study of photoexcited triplet states in polyatomic molecules by the EPR and phosphorescence methods

SOURCE: Izvestiya AN SSSR. Seriya fizicheskaya, v. 27, no. 5, 1963, 634-637

TOPIC TAGS: electron paramagnetic resonance method, phosphorescence method, triplet state EPR signal, hydrocarbon, hetero-atomic substance, photoexcited molecule, higher-order symmetry, benzophenone

ABSTRACT: By using the electron paramagnetic resonance and phosphorescence methods, the lifetime of phosphorescence and the spectra of several hydrocarbons and hetero-atomic substances have been investigated at 77K in solutions of hexane, isopropyl and ethyl alcohol, isopentane, and in solid matrices of polystyrene and methyl methacrylate. It was found that: 1) All the substances and matrices investigated exhibit the presence of EPR signals of triplet states for the transitions $\Delta M = \pm 2$. 2) The frozen solutions of photoexcited molecules in a carefully purefied ethyl alcohol give the strongest signals. 3) The weak dependence

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L 14959-63
ACCESSION NR: AP3000315

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of the signal shapes and widths on the molecular structures is the result of orientation anisotropy present in the aromatic molecules. 4) The interdependence between H_1, the intensity of a magnetic field at a point of maximum absorption line slope, and D_1, the magnitude of a triplet level splitting, can be expressed by a simple analytic formula for the molecules possessing the axes of third- or higher-order symmetry and a single triplet level doubly degenerated. 5) Changes in molecular concentration of 10^{-4}—10^{-2} do not modify the signal intensities, whereas the phosphorescence spectra become more and more diffuse. 6) Evaluation gives 0.1 cm^{-1} as the approximate magnitude of triplet-level splitting in a zero field. 7) The solutions in ethyl alcohol of many substances exhibit decreases up to 50% in signal intensity after being irradiated by light for five minutes; however, all the matrix solutions investigated indicated the presence of radicals whose signal intensities grew with the duration of exposure to light. 8) Signal intensities of radicals formed by the filtered light irradiation of solutions of luminophors in alcohol increase; this phenomenon is singularly connected with a decrease in signal intensity of triplet states. 9) When irradiated with unfiltered light, two-component systems of ethyl alcohol and polymethylmethacrylate, and naphthalene, phenanthrene, and N-ethyl-acridone exhibit considerable increases in EPR signal intensities (300 to 400%). The increases are a function of benzophenone concentration.

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NURMUKHAMETOV, R.N.; SHIGORIN, D.N.; KOZLOV, Yu.I.

Luminescence spectra of solutions of indigo and some of its derivatives at 77°K. Izv. AN SSSR Ser. fiz. 27 no.5:686-689 My '63. (MIRA 16:6)

(Indigo—Spectra)

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24.3500

S/076/63/037/002/010/018
B101/B186

AUTHORS: Shcheglova, N. A., ~~Shigorin, D. N.,~~ Ryabchikova, T. S., Dokunikhin, N. S., Moiseyeva, Z. Z. (Moscow)

TITLE: Study of the luminescence spectra of some anthraquinone carboxylic acid derivatives at low temperatures

PERIODICAL: Zhurnal fizicheskoy khimii, v. 37, no. 2, 1963, 371-377

TEXT: The luminescence spectra of the following compounds were studied in n-hydrocarbon solutions or in the powder: anthraquinone-α-carboxylic acid and its methyl ester, anthraquinone-β-carboxylic acid and its methyl ester, anthraquinone-1,4-dicarboxylic acid and its dimethyl and diethyl esters, 7-chloro-anthraquinone-2-carboxylic acid and its methyl ester, 7-fluoro-anthraquinone-2-carboxylic acid and its methyl ester, 6-fluoro-anthraquinone-2-carboxylic acid and its methyl ester, and 6-chloro-anthraquinone-2-carboxylic acid. Results: The luminescence spectra of the esters and their halogen derivatives at 77°K have a fine vibration structure. The carbonyl of the anthraquinone ring had the highest frequency. The multiplicity of the spectra proved to be highly dependent

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on the length of the hydrocarbon chain of the solvent (n-hexane, n-heptane, n-octane, n-nonane) which fact can be used in the analysis of these compounds. Each substituent being an auxochrome (F, Cl, COOH, $COOCH_3$) has a specific effect on the spectrum, manifest in line shifts and intensity changes of the major peaks. The luminescence spectra of the powdered halogen derivatives of the acids as well as the esters had no fine structure at 77°K, but a system of narrow bands shifted toward the longwave region. The interdistance between the centers of these bands equals the carbonyl frequency of anthraquinone. In powdered 1,4-anthraquinone dicarboxylic acid, reversible self-extinction of the luminescence was observed. This effect disappeared in dioxane solution. The self-extinction is explained by intermolecular interaction (and photo transfer) of one carboxyl proton with the p electrons of the oxygen in the anthraquinone carbonyl group, which effect electron excitation by $p \longrightarrow \pi^*$ transition. This assumption was confirmed by measuring the IR frequency of the carbonyl group. There are 2 figures and 3 tables.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physicochemical Institute imeni L. Ya. Karpov)

SUBMITTED: November 16, 1961

KOZLOV, Yu.I.; SHIGORIN, D.N.; NURMUKHAMETOV, R.N.; PUCHKOV, V.A.

Phototransfer of a proton in the quasiaromatic ring with H-bonding. Zhur. fiz. khim. 37 no.11:2432-2444 N'63.
(MIRA 17:2)

1. Fiziko-khimicheskiy institut imeni L.Ya. Karpova, Moskva.

KOZLOV, Yu.I.; MUROMTSEV, V.I.; PISKUNOV, A.K.; SHIGORIN, D.N.; OZEROVA, G.A.;
VEREYN, N.V.

Formation of radicals via the triplet state in the ultraviolet irradiation of frozen solutions of aromatic molecules. Zhur. fiz. khim. 37 no.12:2800-2802 D '63. (MIRA 17:1)

1. Fiziko-khimicheskiy institut imeni Karpova.

SHIGORIN, D.N.; SHAPET'KO, N.N.; SKOLDINOV, A.P.; RYABCHIKOVA, T.S.

Nature of the hydrogen bond in systems with π-electrons and its effect on the proton magnetic resonance. Dokl. AN SSSR 148 no.5:1141-1144 F '63. (MIRA 16:3)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova. Predstavleno akademikom V.A.Karginym.

(Hydrogen bonding)

(Nuclear magnetic resonance and relaxation)

SHIGORIN, D.N.; SKOLDINOV, A.P.; RYABCHIKOVA, T.S.

Determination of the formation energy of a quasiaromatic cycle with an H-bond from molecular infrared spectrum data. Dokl. AN SSSR 149 no.2:341-344 Mr '63. (MIRA 16:3)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova. Predstavleno akademikom V.A.Karginym.
(Hydrogen bonding) (Molecular spectra)

LOKSHIN, B. V.; PISKUNOV, A. K.; KAZITSYNA, L. A.; SHIGORIN, D. N.

Analysis of the structure of certain chelate compounds by the electron paramagnetic resonance method. Izv. AN SSSR. Ser. fiz. 27 no.1:75-77 Ja '63. (MIRA 16:1)

1. Khimicheskiy fakul'tet Moskovskogo gosudarstvennogo universiteta im. M. V. Lomonosova.

(Chelates—Spectra)
(Paramagnetic resonance and relaxation)

SHIGORIN, D.N.; SHCHEGLOVA, N.A.; PISKUNOV, A.K.; OZEROVA, G.A.;
DOKUNIKHIN, N.S.

H-bonds in excited electronic states of molecules with π-electrons. Dokl. AN SSSR 150 no.4:862-865 Je '63.
(MIRA 16:6)

1. Fiziko-khimicheskiy institut imeni L.Ya. Karpova.
Predstavleno akademikom A.N. Tereninym.
(Molecular spectra)
(Hydrogen bonding)

L 32069-66 EWT(m)/EWP(j) RM

ACC NR: AR6016172 SOURCE CODE: UR/0058/65/000/011/D012/D012

AUTHOR: Shigorin, D. N.; Shcheglova, N. A.; Piskunov, A. K.; Ozerova, G. A. 44

TITLE: Hydrogen bonds in excited electronic states of molecules with π-electrons B

SOURCE: Ref. zh. Fizika, Abs. 11D83

REF SOURCE: Tr. Komis. po spektroskopii. AN SSSR, t. 3, vyp. 1, 1964, 302-312

TOPIC TAGS: hydrogen bonding, excited state, absorption spectrum, luminescence spectrum, nonmetallic organic derivative, conjugate bond system, ground state, luminescence quenching

ABSTRACT: On the basis of data on the absorption and luminescence spectra of α-oxy- and methoxy-derivatives of anthraquinone it is shown that the energy of production of the hydrogen bond in the excited state increases compared with the ground state by a factor of almost 2 and reaches 15 kcal. The increase in the energy of the H bond in the case of excitation with conjugated bonds is connected with the increase of the energy of the π-electron interaction in the quasiaromatic cycle, formed with participation of the p-orbit of the hydrogen atom of the X-H group. The question of the role of the H bond in processes of deactivation of the triplet state and luminescence quenching is considered. [Translation of abstract]

SUB CODE: 20, 07

Card 1/1 90

L 33155-66 EWT(m)/EWP(j) RM

ACC NR: AR6016177 SOURCE CODE: UR/0058/65/000/011/D014/D014

AUTHOR: Shigorin, D. N.; Gastilovich, Ye. A.; Komarov, N. V.

40
B

TITLE: Investigation of compounds of the group $(CH_3)_3\text{-X-C}{\equiv}\text{CH}$, where X = C, Si, Sn, and Pb in the region of valence oscillations of the groups C-C and C-H

SOURCE: Ref. zh. Fizika, Abs. 11D97

REF SOURCE: Tr. Komis. po spektroskopii. AN SSSR., t. 3, vyp. 1, 1964, 673-678

TOPIC TAGS: absorption band, ir spectrum, complex molecule, molecular physics, molecular interaction

ABSTRACT: The frequencies of the valence oscillation groups C≡C and ≡C-H in compounds $(CH_3)_3\text{-X-C}{\equiv}\text{H}$ were calculated. The calculated frequencies are compared with the measured frequencies in ir spectra of the compounds $(CH_3)_3\text{-C-C}{\equiv}\text{CH}$ (I), $(CH_3)_3\text{-Si-C}{\equiv}\text{CH}$ (II), and $(C_2H_5)_3\text{-SnC}{\equiv}\text{CH}$ (III). It is concluded that in compounds with Si, Ge, Sn, and Pb there should be observed an intramolecular interaction with participation of the π-electrons of the C≡C bond, using the d-orbit of the X atom. The presence of such an interaction is confirmed experimentally by the fact that an increase is observed in the intensity of the absorption band of the group C≡C in II and in III compared with I, and that compounds II and III form stronger complexes with an electro-donor solvent: $(CH_3)_3\text{-X-C}{\equiv}\text{CH----Y-R}$. [Translation of abstract]

SUB CODE: 07, 20

LS

Card 1/1

ZHURAVLEVA, T.S.; PETROV, E.S.; SHIGORIN, D.N.

Electron paramagnetic resonance spectrum of the anion radical of diphenylacetylene. Zhur. strukt. khim. 5 no.5:785-786 S-O '64 (MIRA 18:1)

1. Fiziko-khimicheskiy institut imeni L. Ya. Karpova.

ALEKSANDROVA, I.P.; SHIGORIN, D.N.; SKOLDINOV, A.P.

X-ray spectra of quasi-aromatic inner-complexes of copper. Zhur. fiz. khim. 38 no.5:1203-1209 My '64. (MIRA 18:12)

1. Fiziko-khimicheskiy institut imeni Karpova. Submitted June 8, 1963.

SHCHEGLOVA, N.A.; SHIGORIN, D.N.

Particular features of the electronic spectra of 1,4-naphthoquinone and some of its derivatives. Zhur. fiz. khim. 38 no.5:1261-1267 My '64. (MIRA 18:12)

1. Fiziko-khimicheskiy institut imeni Karpova. Submitted Aug. 9, 1963.

L 8750-65 EWG(j)/EPA(s)-2/EWT(m)/EPF(c)/EPR/EWP(j)/T/EWA(h)/EWA(1) Pc-4/Pr-4/
Ps-4/Pt-10/Peb ASD(m)-3/RAEM(i)/ASD(p)-3/ESD(t) RM/WW
ACCESSION NR: AP4043779 S/0190/64/006/008/1411/1414

8

AUTHOR: Nurmukhametov, R. N.; Bondareva, L. V.; Shigorin, D. N.; Tokareva, L. G.; Mikhaylov, N. V.

TITLE: Application of the luminescence method to determine the state of stabilizing additives in polymers 15

SOURCE: Vy*sokomolekulyarny*ye soyedineniya, v. 6, no. 8, 1964, 1411-1414

TOPIC TAGS: di-β-naphthyl-n-phenelenediamine, di-β-naphthyl-n-phenelenediamine antioxidant, antioxidant, polypropylene fiber, polyamide fiber, di-β-naphthyl-n-phenelenediamine luminescence spectra, polymer additive, photooxidation inhibitor, polymer stabilizer, synthetic fiber

ABSTRACT: A study is made of the absorption and luminescence spectra of N,N'-di-2-naphthyl-p-phenylenediamine 7 (I) used as a stabilizing additive possessing a light- and heat-protective action on polypropylene 15 and polyamide fibers. 15 From identifications of the luminescence spectra of solutions and fibers containing the addi-

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L 8750-65

ACCESSION NR: AP4043779

tive it was concluded that a solid molecular solution is formed with the addition of I to the polymer. The fibers and solutions containing I were subjected to heat treatment and to gamma and ultraviolet irradiation. The consumption of I in the polymers was determined by recording the intensity of the initial fluorescence band. Solutions of I had absorption bands in the near UV region. The primary protective effect of I is related to its function as a filter absorbing the UV section of the light. The photochemical inhibiting effect according to Semenov is based on the termination of the reaction caused by free radicals. With the absorption of light and gamma quanta, and also with heat treatment, a molecule of I gives up an electron easily and various positive ions and ion radicals are formed. As a result of these treatments colored products are formed from I. It is assumed that the primary photochemical act in I was the photoionization, which apparently proceeds through the triplet state. From the ease with which the photooxidation of molecules of I occurred, it can be concluded that I is a strong antioxidant capable of inhibiting photooxidation processes in polymers. It can be seen from the observed similarity in the change of

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ACCESSION NR: AP4043779 2

fluorescence in fibers with stabilizing additives during UV or gamma irradiation and during heating in nitrogen, that there is a far-reaching analogy in the mechanism of photochemical and thermal destruction of polymers. Orig. art. has: 4 figures.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physicochemical Institute)

SUBMITTED: 15Aug63 ATD PRESS: 3113 ENCL: 00

SUB CODE: OC, GC NO REF SOV: 012 OTHER: 002

Card 3/3

GASTILOVICH, Ye.A.; SHIGORIN, D.N.; KOMAROV, N.V.

Use of the method of infrared absorption spectra in studying acetylene derivatives containing elements of group IV of Mendeleev's periodic law. Opt. i spektr. 16 no.1:46-51 Ja '64. (MIRA 17:3)

SHAPET'KO, N.N.; SHIGORIN, D.N.; SKOLDINOV, A.P.; RYABCHIKOVA, T.S.; RESHETOVA, L.N.

Chemical shifts of nuclear magnetic resonance of protons of O--H compounds forming an intramolecular hydrogen bond of the O--H...O type. (MIRA 17:10)
Opt. i spektr. 17 no.3:459-461 S '64.

ACCESSION NR: AP4019525 S/0076/64/038/002/0469/0471

AUTHOR: Smirnova, V. I.; Zhuravleva, T. S.; Shigorin, D. N.; Gracheva, Ye. P.; Shostakovskiy, M. F.

TITLE: EPR spectra of some di-substituted acetylenes upon exposure to gamma rays and to light

SOURCE: Zhurnal fizicheskoy khimii, v. 38, no. 2, 1964, 469-471

TOPIC TAGS: methylphenylacetylene structure, ethylphenylacetylene structure, dimethylacetylene structure, electron paramagnetic resonance, acetylene, alkyl radical, acrylic compound, methyl, EPR

ABSTRACT: This is a continuation of a work by the same authors (AN SSSR, Dokl., 140, 149, 1961) where they described how a number of acetylenes of the $RC \equiv CH$ type (where R is an alkyl radical) upon exposure to gamma radiation form radicals where the unpaired electron is delocalized by the triple bond over the whole molecule. The present work transfers the above study to $Ar - C \equiv C - R$ arylic compounds of a different structure. The object of the study were: methylphenylacetylene, its deuterium tagged form, ethylphenylacetylene and dimethylacetylene.

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ACCESSION NR: AP4019525

UV radiation was provided by the SVDSh - 1000 lamp. Gamma doses were 2 to 80 m. rad. Using the EPR method, the structure of radicals formed by gamma and light radiation of the above compounds was determined; the radicals are formed by tearing off a hydrogen atom from the methyl or methylene group. In these radicals the free electron is basically localized in the R group, whereas in the $R - \equiv C - CH_2$ radical (like the propynyl radical $CH_2 = C = CH.$) the unpaired electron is delocalized by the triple bond over the whole molecule. Orig. art. has: 5 figures, 2 formulas, 1 table.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physics and Chemistry Institute)

SUBMITTED: 08Feb63	DATE ACQ: 31Mar64	ENCL: 00
SUB CODE: GC, GP	NO REF SOV: 001	OTHER: 000

Card 2/2

S/0076/64/038/003/0742/0745

ACCESSION NR: AP4033409

AUTHORS: Smirnova, V.I.; Zhuravleva, G.S.; Yanova, K.G.; Shigorin, D.N.

TITLE: Electron paramagnetic resonance study of the structure and behavior of radicals formed on γ-, β-, and photolytic irradiation of acetaldehyde and formaldehyde

SOURCE: Zhurnal fizicheskoy khimii, v. 38, no. 3, 1964, 742-745

TOPIC TAGS: electron paramagnetic resonance, free radical, acetaldehyde, formaldehyde, beta irradiation, gamma irradiation, ultraviolet irradiation

ABSTRACT: The structure and behavior of free radicals formed upon β-, γ- and ultraviolet irradiation of acetaldehyde and upon β- and γ- irradiation of formaldehyde were studied by the electron paramagnetic resonance (EPR) method. The studied compounds were condensed from the gaseous phase into special ampules and were irradiated at -190C. Upon irradiation of acetaldehyde with β-ray doses of 3 million rads, a singlet is obtained, which is attributed to the

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ACCESSION NR: AP4033409

breakage of the C-C bond and formation of CH_3 and $CH\dot{O}$ radicals, where CH_3 radicals rapidly recombine but CHO radical has a localized unpaired electron and consequently it does not possess nuclear magnetic moment. At doses of 40 to 100 million rads a triplet with 2 additional less intense lines is observed and is attributed to the supposition of the singlet and quartet obtained at doses of 3 million rads. The line width was $\Delta H = 47.0$ oersted. Upon increase of the temperature from -130 to -120C the singlet disappears and the quartet becomes symmetrical. It was assumed that the quartet appears upon the breakage of C-H bond with the formation of $CH_3-C=O$ radicals or upon the breakage of the C-O bond in the polymeric chain with the formation of $O-\underset{\underset{CH_3}{|}}{C}-O$ radical. The quenching temperature of the quartet was -105 to -50C. On β-irradiation of formaldehyde at doses of 7 million rads the doublet formed is related to the formation of -O-CH-O- type radical. At doses of 70 million rads the spectrum appears as an assymetrical line with shoulders which may be composite of two different spectra of the -O-CH-O- (doublet) and

ACCESSION NR: AP4033409

$-CH_2-O-CH_2$ radicals (triplet). At 7 million rad dose side signals had a separation of 125 oersted with the central doublet of 13 oersted between its components. Beta irradiation of polyformaldehyde produces a triplet which is attributed to $-CH_2-O$ or CH_2-O-CH_2 radicals. It was concluded that the nature of radicals formed on irradication of acetaldehyde does not depend on the aggregate state of the compound and that the temperature of radical quenching apparently depends on the aggregate state of the acetaldehyde monomer. Orig. art. has: 4 figures

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut (Scientific Research Institute of Physical Chemistry)

SUBMITTED: 14Mar63

ENCL: 00

SUB CODE NP

NR REF SOV: 004

OTHER: 002

Card 3/3

SIMONOV, A.P.; SHIGORIN, D.N.

Infrared absorption spectrum and structure of crystalline lithium methylate. Opt. i spektr. 17 no.6:848-858 D '64.
(MIRA 18:3)

L 20106-65 EWT(m)/EWP(j) Pc-4 BSD/SSD(c)/AFWL/ASD(a)-5/AS(mp)-2/APGC(b)/ESD(gs)
ACCESSION NR: AP4044439 RM S/0076/64/038/008/1963/1972

AUTHOR: Shcheglova, N. A. (Moscow); Shigorin, D. N. (Moscow); Dokunikhin, N. S. (Moscow) B

TITLE: Luminescence and absorption spectra of alpha and beta hydroxyanthraquinones

SOURCE: Zhurnal fizicheskoy khimii, v. 38, no. 8, 1964, 1963-1972

TOPIC TAGS: hydroxyanthraquinone, absorption spectrum, luminescence spectrum, hydrogen bond, molecular excitation

ABSTRACT: The luminescence and absorption spectra of α- and β-hydroxy, dihydroxy and tetrahydroxyanthraquinones and some of their methoxy derivatives in normal hydrocarbons were investigated in order to study the spectra of compounds, containing intramolecular hydrogen bonds and their manifestation in the excited electronic state. It was found that the shape and position of luminescence and absorption bands of a number of hydroxyanthraquinones and some of their methoxy substituted derivatives in n-hydrocarbons at 77K depend on the number and position of the hydroxy groups in the anthroquinone ring. The luminescence spectra

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L 20106-65
ACCESSION NR: AP4044439

of α-hydroxy, 1,5-dihydroxy, β-hydroxy and 2,6-dihydroxyanthraquinones are washed out and shifted toward the red. The washed-out nature of spectra is closely related to the shortened lifetime of the excited state of hydroxyanthraquinones as compared with anthraquinone. Both the luminescence and the absorption spectra of 1,4-dihydroxy, 1,2,5,8- and 1,4,5,8-tetrahydroxyanthraquinones have a vibrational fine structure. For these substances the established frequencies of purely electronic transitions are 19115 cm^{-1}, 18774 cm^{-1} and 17667 cm^{-1} respectively. The H bond has a significant effect on the nature of the excited state of the molecule. From the comparison of the spectra of α-hydroxy and α-methoxyanthraquinones it is apparent that the formation of H bond leads to the long wave length shift of absorption and luminescence spectra and also to the increase of the intensity of the long wavelength absorption bands. The energy of the H bond has been determined in the excited state for α-hydroxy derivatives of anthraquinones. The energy of the H bond greatly increases during the transition of the molecule into the excited electronic state, which is explained by the increase of the energy of π-electron interaction during the formation of quasiaromatic ring with H bond. Orig. art. has: 6 tables and 4 figures.

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L 20106-65
CCESSION NR: AP4044439

SSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Institute of Physical Chemistry)

SUBMITTED: 21Aug63 ENCL: 00

SUB CODE: GC, OP NO REF SOV: 012 OTHER: 008

Card 3/3

SHIGORIN, D.N.; SKOLDINOV, A.P.; RYABCHIKOVA, T.S.; GOLDER, G.A. (Moscow)

Infrared spectra of pseudoaromatic cycles with H-bonding at low temperatures. Zhur.fiz.khim. 38 no.8:1996-2001 Ag '64. (MIRA 18:1)

1. Fiziko-khimicheskiy institut imeni L.Ya.Karpova.

L 16195-65 EWT(m)/EPF(c)/EWP(j) Pc-4/Pr-4 RPL WW/JFW/RM
ACCESSION NR: AP4046084 S/0076/64/038/009/2279/2283
B

AUTHOR: Shigorin, D. N.; Piskunov, A. K.; Ozerova, G. A.; Shcheglova, N. A.
Vereyn, N. V.

TITLE: The role of H-bonds in processes of deactivating activated states of molecules leading to the formation of radicals

SOURCE: Zhurnal fizicheskoy khimii, v. 38, no. 9, 1964, 2279-2283

TOPIC TAGS: H bond, activated molecule, deactivation, radical formation, radical formation mechanism, intermolecular radical formation, EPR spectrum, luminescence

ABSTRACT: The mechanism of radical formation and the role of H-bonds therein was investigated in processes embodying intermolecular radical formation-- when the activated molecules form complexes among themselves or with molecules of the media. The EPR spectra and the luminescence were examined of a series of systems: N-ethylacridone, anthraquinone and some of its derivatives, triphenylamine, and carbazole, in different media in a molar ratio of 1:1 with $c=10^{-3}$ mol/l.

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L 16195-65

ACCESSION NR: AP4046084

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Photo-illuminated powders under vacuum at 77K gave no EPR signal. In samples crystallized from ethanol and in luminophor systems X: . . . H-O-R, a singlet appeared whose intensity increased proportionally to the intensity of illumination. Photoactivation of systems with the luminescent chromophore $>C=O$ gave a singlet and EPR spectra corresponding to radicals of the solvent. Photoactivation of systems containing the chromophoric atom $\geqslant N$, gave a weak singlet and intense spectra of the solvent radical (radical yield $\sim I^n$, $n \approx 2$). If the $\geqslant N$ atom which formed a H-bond with the O-H groups did not affect the electron excitation, the radical yield was small. In solvents (hydrocarbons) which did not contain the X-H group capable of forming H-bonds, the luminophores did not give noticeable EPR signals. It was concluded the H-bond played an important role in the process of forming radicals from a matrix as a result of deactivating activated states of a molecule. This is a two-stage process (see enclosed figure). Formation of the radical complex takes place in the first stage as a result of the transition of the H atom from the molecule of the matrix to the luminophore molecule due to absorption of a quantum of light in $S \rightarrow S^* \rightsquigarrow T$ transitions. The radical complex is decomposed in the second stage forming radicals of the matrix due to absorption

L 16195-65
ACCESSION NR: AP4046084

of a quantum of light in the $S_R \rightarrow S_R^*$ transition. A network of matrix molecules connected by H-bonds is necessary for this. The yield of radicals in the overall process is proportional to the light intensity I^n, where $n \leq 2$. The triplet activated state does not take part in the process of formation of radicals from the matrix. Orig. art. has: 1 table and 4 figures.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physical Chemical Institute)

SUBMITTED: 11Oct63 ENCL: 01

SUB CODE: GC NO REF SOV: 005 OTHER: 000

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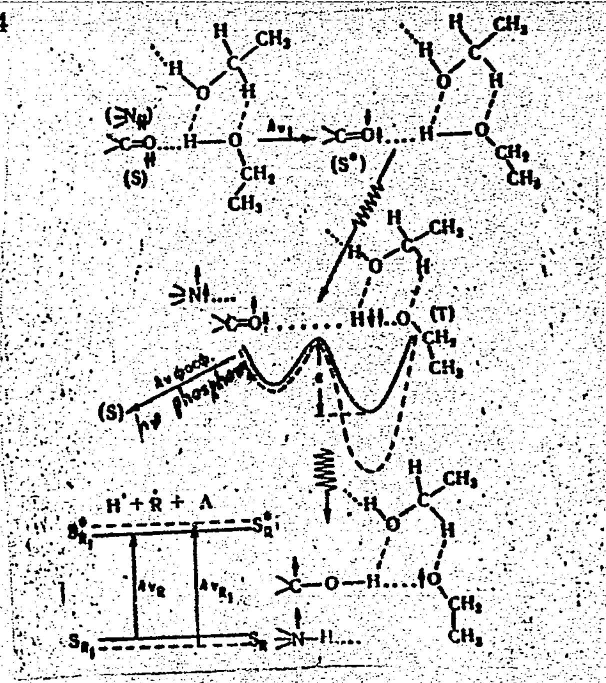
L 16195-65

ACCESSION NR: AP4046084

ENCLOSURE: 01 0



Card 4/4

PISKUNOV, A.K.; KHOLMOGOROV, V.Ye.; SHIGORIN, D.N.; VEREYN, N.V.; OZEROVA, G.A.

Mechanism underlying the formation of radicals during photoirradiation of triphenylamine ethanol solutions frozen at 77° K. Dokl. AN SSSR 154 no.4:910-913 F '64. (MIRA 17:3)

1. Fiziko-khimicheskiy institut im. L.Ya. Karpova. Predstavleno akademikom A.N. Tereninym.

ACCESSION NR: AP4040960 S/0020/64/156/005/1174/1177

AUTHOR: Terent'yev, A. P.; Panova, G. V.; Shigorin, D. N.; Rukhadze, Ye. G.

TITLE: EPR spectra of optically-active chelate compounds of copper with oxyaldimines and oxyketimines

SOURCE: AN SSSR. Doklady*, v. 156, no. 5, 1964, 1174-1177

TOPIC TAGS: EPR, EPR spectrum, chelate compound, optically-active chelate compound, copper, copper compound, copper chelate compound, aldimine compound, ketimine compound, copper-oxyaldimine compound, copper-oxyketimine compound

ABSTRACT: It is a well-known fact that the degree of delocalization of an unpaired electron can be studied directly by the electron paramagnetic resonance method. Hence, one and the same structural peculiarities of molecules can be found in the optical activity and EPR spectra. With this in mind, the authors studied the EPR spectra of the titled chelate compounds of copper. The analysis was carried out on a superheterodyne EPR spectrometer with a frequency of 9455 mc. All of the compounds in a chloroform solution produce EPR spectra which are characterized by four lines of a superfine structure, which originate as the result of the interaction of the copper atom's nuclear moment ($I_{Cu} = 3/2$) with the

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