STUDIES IN THE FIELD OF 2,1,3-THIA- AND -SELENADIAZOLES

LVI. Structure and Reactivity of Benzo-2,1,3-thia- and -selenadiazoles*

V. G. Pesin

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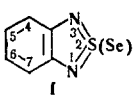
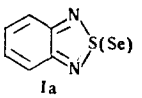
The results of studies on 2,1,3-thiadiazole, benzo-2,1,3-thiadiazole, benzo-2,1,3-selenadiazole, and their derivatives by chemical, physicochemical, and physical methods give no grounds for assuming that they have a quinoid structure. These results permit the statement that these heterocycles containing quatervalent sulfur or selenium are typical heteroaromatic systems satisfying Hückel's (4n + 2) rule.

At the present time there is no single opinion on the question of the structure of benzo-2,1,3-thia- and -selenadiazoles.

The synthesis of benzo-2,1,3-thia- and -selenadiazoles (I) from o-phenylenediamine and sulfur dioxide or selenium dioxide [2], and also the high stability of them to the action of oxidizing agents, high temperatures, acid, and alkalis, may serve as a proof of structure I.



I

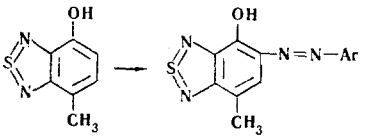


Ia

Luzzati [3, 4] used X-rays to determine the interatomic distances in benzo-2,1,3-thia- and -selenadiazoles. It is the author's opinion that the benzoic (I) and quinoid (Ia) structures are equiprobable for benzo-2,1,3-thiadiazoles. According to these data, benzo-2,1,3-selenadiazole is best represented by the quinoid (Ia) structure. Efros and his associates—relying on the Luzzati data, as well as on their own research—came to the conclusion that benzo-2,1,3-thia- and -selenadiazoles exhibit the quinoid (Ia) structure [5–11]. Baker and Ollis [63] also regard the quinoid (Ia) structure as the most likely. Weinstock [16] came to the conclusion that the structure was benzoic (I).

Our investigations of benzo-2,1,3-thiadiazole and benzo-2,1,3-selenadiazole and their derivatives have shown that these heterocyclic systems possess a well-marked aromatic nature which is fully comparable with the aromaticity of naphthalene [68].

In electrophilic substitution reactions the substituent enters position 4 (7) preferentially; similarly, the α-position in naphthalene is more reactive than the β-position. On azo coupling, the azo group occupies position 4 (7) and does not enter position 5 if position 4 (7) is free [5, 7, 19]. However, as in the case of 1-hydroxy-4-methylnaphthalene [20], if both positions 4 and 7 are occupied the azo group replaces the hydrogen in position 5 [21, 22].



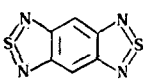
In a similar manner to α- and β-nitronaphthalenes, 4- and 5-nitrobenzo-2,1,3-thiadiazoles readily take part in nucleophilic replacement of hydrogen by an imino group [18, 69] (nitrobenzene does not take part in this reaction).

Like naphthalene, benzo-2,1,3-thiadiazole possesses some unsaturation, which is expressed in the capacity for addition of chlorine, bromine, and ozone under the usual conditions [64–65]. Amino- and hydroxybenzo-2,1,3-thiadiazoles take part in the Bucherer reaction [12, 13]; 4- and 5-hydroxybenzo-2,1,3-thiadiazoles are esterified by alcohols in the presence of concentrated sulfuric acid [14]; these reactions take place in the naphthalene series, but not with aniline and phenol.

However, the unsaturated properties of benzo-2,1,3-thiadiazole are limited. Benzo-2,1,3-thia- and -selenadiazoles do not take part in the diene synthesis with maleic anhydride [5, 15, 17].

Benzo-2,1,3-selenadiazole and its methyl derivatives, unlike their thio analogs, do not add halogens [66]. The selenadiazole ring has considerably less influence than the thiadiazole ring on the reactivity of the benzene nucleus in electrophilic substitution reactions as, for example, in nitration and halogenation [66]. In this sense it is possible to speak of the more pronounced aromatic nature of benzo-2,1,3-selenadiazole as compared with its thia analog. This can be explained by the difference in the structure of the electron shells of sulfur and selenium. The latter has a greater capacity than sulfur for extending its valence shell to ten electrons through the vacant d-orbitals.

An important piece of evidence against a quinoid structure of benzo-2,1,3-thiadiazole is the existence of a three-ring system [18]:



The similarity in the benzo-2,1,3-thiadiazole series and the series of condensed benzene hydrocarbons is found on comparing anthracene and naphthalene, on the one hand, with naphtho[2,3-d]-[2,1,3]-thiadiazole (II) [23] and benzo-2,1,3-thiadiazole, on the other.

*For part LV, see [1].

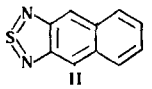
Table 1

Positions of the Absorption Bands of the C—C and C—H Bonds for Substituted Benzenes and Benzo-2, 1, 3-thiadiazoles

Type of vibration	Range of frequencies, cm^{-1}	
	substituted benzenes	substituted benzo-2,1,3-thiadiazoles
C–C stretching	1620—1560 1600—1560 1525—1475 1470—1440	1610—1583 1570—1535 1546—1506 1486—1455
Deformation (nonplanar)	1,2*	$C_6H_4N_2S$
	770—735	744 755
	1,2,3*	4*
	810—750 725—680	800 750
	1,2,4*	5*
	860—800 750—700 900—860	816—802 750 860

Type of vibration	Range of frequencies, cm^{-1}	
	substituted benzenes	substituted benzo-2,1,3-thiadiazoles
C–H deformation (planar)	1,2*	$C_6H_4N_2S$
	1225—1175 1125—1090 1070—1000 1000—960	1230 1130 1043.10 982
	1,2,3*	4*
	1175—1125 1110—1070 1070—1000 1000—960	1150—1140 1085—1075
	1,2,4*	5*
	1225—1175 1175—1125 1125—1090 1070—1000 1000—960	1250—1220 1130 1045—1014 930

*Positions of the substituents.

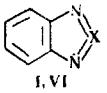
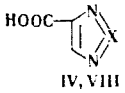
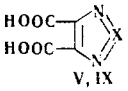
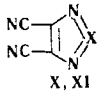


II

It is known that anthracene is less aromatic than naphthalene. Analogously, the naphthothiadiazole II is less aromatic than benzo-2,1,3-thiadiazole. In contrast to the latter, which does not react with maleic anhydride, the naphthothiadiazole II does react with it and also with phenylmaleimide under the usual conditions (boiling benzene), with the formation of the corresponding adducts. It has also been shown that the naphthothiadiazole II is a less reactive diene in the Diels-Alder reaction than anthracene, which clearly shows that it has a greater aromaticity than anthracene.

Table 2

UV Spectra

Compound	X=S	X=CH—CH
	λ_{max}, nm (log ε)	λ_{max}, nm (log ε)
 I, VI	311 (4.14) 305 (4.14) 223.5 (4,25)	313 (3.77) 306 (3.76) 232 (4.45)
 III, VII	255 (3.89)	261 (3.82)
 IV, VIII	263 (4.01)	268 (3.95)
 V, IX	266 (3.95)	279 (3.85)
 X, XI	272 (4.0)	274 (3.8)

Analogously, benzo-2,1,3-thiadiazole is more aromatic than naphthalene; the latter takes part in the diene synthesis with maleic anhydride under the usual conditions [24].

The greater aromaticity and smaller degree of "unsaturatedness" of benzo-2,1,3-thiadiazole as compared with naphthalene is also shown in the behavior of these compounds under the conditions of homolytic substitution. Benzo-2,1,3-thiadiazole does not react with N-bromosuccinimide in boiling carbon tetrachloride or in the melt (95–100° C) [25], the latter compound being a specific reagent for allyl bromination under these conditions. Under the same conditions, naphthalene forms 1-bromonaphthalene in 77% yield [26, 27].

The electronic spectra of benzo-2,1,3-thiadiazole and its derivatives are similar to the typical spectra of condensed aromatic compounds [28].

The IR spectra of benzo-2,1,3-thiadiazole and its derivatives also show a well-marked aromatic nature. This can be seen, for example, from a comparison of the frequencies of the C—C and C—H bonds of the vibrational spectra of benzo-2,1,3-thiadiazole and its 4- and 5-substituted derivatives (X = CH_3, Cl, Br) with the corresponding frequencies for benzene and its derivatives [29] (Table 1).

Weinstock [16] compared the electronic spectra of benzo-2,1,3-thiadiazole (I), 2,1,3-thiadiazole (III), and 2,1,3-thiadiazole-3-carboxylic and -3,4-dicarboxylic acids (IV and V) with the electronic spectra of quinoxaline (VI), pyrazine (VII), and pyrazine-2-carboxylic and -2,3-dicarboxylic acids (VIII and IX). He also compared the dissociation constants of the acids IV, V, VIII, and IX, and thus demonstrated the great similarity of these compounds. The behavior of compounds I, VI, III, and VII under polarographic reduction conditions also shows their similarity.

The electronic spectra of derivatives of benzo-2,1,3-thiadiazole and of quinoxaline [30–32] are also characterized by a pronounced similarity.

Table 2 gives data on the UV spectra of compounds I, VI, III, VII, IV, VIII, V, and IX and of the dinitriles corresponding to the acids V and IX (X and XI).

The PMR spectra of the heterocycles III and VII are also similar: τ for III is 1.30 and for VII 1.40 [47].

Benzo-2,1,3-thiadiazole (I) and quinoxaline (VI) are also similar in a number of chemical properties. For example, the action of $KMnO_4$ on I and VI forms the dicarboxylic acids V and IX, respectively [16, 33, 34], which undergo decarboxylation on heating, with the formation of the monocarboxylic acids VI and VIII and the heterocycles III and VII [16, 35].

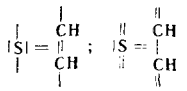
The similarity in the properties of 2,1,3-thiadiazole and pyrazine and those of benzo-2,1,3-thiadiazole and quinoxaline, and of their derivatives, is explained by the capacity of sulfur for increasing its valence shell to two electrons through the vacant d-orbitals [36–38]. In this case the same analogy in properties is observed as for thiophene and benzene [39–41], for naphthalene and benzothiophene [42], for naphthalene and thiophthene [41], and for 1,3-thiazole and pyridine [43]. In all these heterocycles, the sulfur, possessing the characteristic feature of the structure of its electron cloud that has been mentioned, is capable of re-

Table 3

Molecular Structure of 2,1,3-Thiadiazole

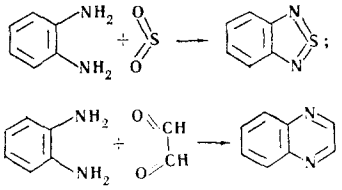
Bond length, Å			H–S–N angle	Method of investigation
C—C	C—N	S—N		
1.413	1.329	1.632	99.4°	Electron diffraction [49]
1.420	1.328	1.631	99.55°	Radiospectroscopy [50]

peating the properties of the vinylene group that depend on the mobile electrons.



Zahradnik and Coutecky [44] employed the MO LCAO method for a comparative study of four isomeric thiadiazoles, using the Longuet-Higgins model and a model taking no account of the participation of the d-orbitals. The authors came to the conclusion that the limited experimental data can be best represented by the results obtained using the Longuet-Higgins model. Plemenkov [70], who calculated molecules of I and **Ia** in the MO LCAO method taking pd-hybridization into account and without it came to the same conclusion. It was shown that the models taking pd-hybridization into account correspond to the actual state of the molecules I and **Ia**.

Hinsberg [2] also turned his attention to the similarity of many of the properties of benzo-2,1,3-thiadiazole and quinoxaline, including the formation of readily hydrolyzable salts and of complex compounds, and even the similar smells of these compounds. Pointing out the similarity in the synthesis of the compounds, this author suggested that sulfur and the =CH—CH= chain were equivalent for these substances:



The broad chemical investigations of 2,1,3-thiadiazole derivatives carried out by Carmack et al. [16, 17, 45–47, 71] have shown that this heterocycle possesses a well-marked aromatic nature and does not exhibit the properties characteristic for dienes; in particular, it does not add bromine or maleic anhydride [16–17].

Electron diffraction and radiospectroscopic investigations of the molecular structure of 2,1,3-thiadiazole [48–50] have shown that the molecule is planar with the lengths of the C—C, C—N, and S—N bonds having values intermediate between those of the corresponding double and single bonds (Table 3).

A comparison of the molecular parameters of thiophene and 1,2,5-thiadiazole led the authors to the conclusion that the replacement of the two carbon atoms in positions 2 and 5 of thiophene by nitrogen had little effect on the total aromaticity. The authors [50] consider that "structure (**IIIa**) more nearly represents the molecular parameters [given in the table] and the principal resonance structure of this molecule."

IIIa

However, in their opinion, this conclusion does not contradict the results of Carmack and his colleagues, since the parameters determined by physical methods (electron diffraction and radiospectroscopy)

Table 4

Double-Bondedness of the Bonds in the Molecules of the Thiadiazoles

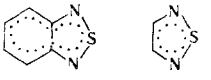
Compound	Bond		
	X—N, X=S, Se	C—N	C—C
2,1,3-Thiadiazole	0.35	0.51	0.40
Benzo-2,1,3-thiadiazole	0.54	0.46	0.35
Benzo-2,1,3-selenadiazole	0.08	0.85	0.17

relate to the gound state of the molecule. Carmack et al. studied properties depending on the mobile electrons, and their conclusion is consequently based on the results of experiments in which, in addition to the ground state, an important role was played by an excited electronic state.

Table 4 gives the degrees of double-bondedness of the S—N, Se—N, C—N, and C—C bonds obtained by comparing the results of X-ray structural studies with the corresponding values for the bonds according to Pauling [51].

Consequently, the structural data agree with the aromatic properties of 2,1,3-thiadiazole and benzo-2,1,3-thiadiazole.

Thus, the results of investigations of 1,2,5-thiadiazole and benzo-2,1,3-thia- and -selenadiazoles and their derivatives by chemical, physicochemical, and physical methods give no grounds for assuming that they possess a quinoid structure. These results permit the statement that the heterocycles containing quatervalent sulfur or selenium are typical heteroaromatic systems satisfying Hückel's (4n + 2) rule [52, 53, 68].

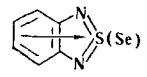


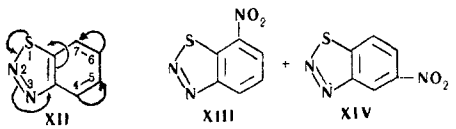
Benzo-2,1,3-thiadiazole nitrates as readily as benzene (0° C, HNO_3 with d 1.35). The influence of the thiadiazole ring is shown only in the direction of substitution: the nitro group enters position 4 (7). However, even this influence is considerably weakened in 4-methyl- and 4-methoxybenzo-2,1,3-thiadiazoles and is not shown at all in 4-hydroxybenzo-2,1,3-thiadiazole [54]. The chlorination and chloromethylation of benzo-2,1,3-thiadiazole form predominantly the 4,7-disubstituted derivatives; when these reactions are carried out with 5,6-dimethylbenzo-2,1,3-thiadiazole, the 4,7-disubstituted derivatives are formed exclusively [52, 53, 67].

Thus, the thiadiazole ring, as an electron-accepting structural element, exerts an extremely weak influence on the reactivity of the benzene ring in reactions with strong electrophilic reagents.

The facts presented can be explained if it is assumed that in the benzo-2,1,3-thiadiazole molecule and the selena analog, the sulfur or selenium and the nitrogen atoms are arranged symmetrically with respect to one another. In this case, there must be

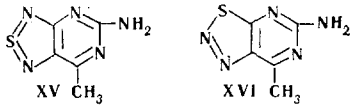
a symmetrical attraction of the electron cloud in the direction of the thiadiazole (or selenadiazole) ring and, as a consequence, a similar impoverishment of the electrons in positions 5 and 6 and an enrichment of those in positions 4 and 7 of the benzene nucleus. This explanation is in agreement with the behavior of the isomeric benzo-1, 2, 3-thiadiazole (XII) under nitration conditions. This heterocycle does not nitrate below 100° C [55]. When it is heated with potassium nitrate in concentrated sulfuric acid at 100° C, a mixture of 5- and 7-nitrobenzo-1, 2, 3-thiadiazoles (XIII) and (XIV) is formed [56].





XII XIII XIV

Such a strong deactivation of the whole benzene nucleus and of positions 5 and 7 to a smaller extent can be explained by the unsymmetrical structure of the 1, 2, 3-thiadiazole ring, which leads to a displacement of the electron cloud in one direction. A similar effect is characteristic for the nitro group in nitrobenzene. This influence of the structure of the thiadiazole ring on the reactivity of the nucleus adjacent to it on nitration is observed also in another electrophilic substitution reaction. 6-Amino-4-methylpyrimido-2, 1, 3-thiadiazole XV readily couples with p-nitrobenzenediazonium chloride even in an acid medium; the isomeric 6-amino-4-methylpyrimido-1, 2, 3-thiadiazole (XVI) does not take part in this reaction [57].

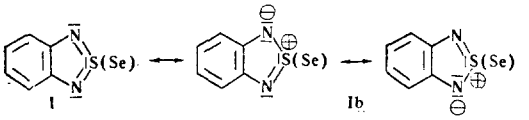


XV XVI

It is clear that the lower nucleophilicity of the carbon of the methyl group in compound XVI is due to the one-sided and, consequently, stronger electron-attracting influence of the 1, 2, 3-thiadiazole ring as compared with the 2, 1, 3-thiadiazole ring in compound XV.

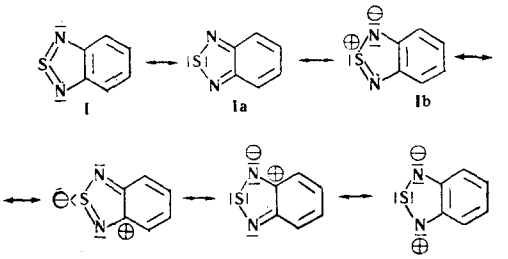
A comparison of the dipole moments of benzo-2, 1, 3-thiadiazole (1.73) [58] and nitrobenzene (3.97) [59, 60] also shows the relatively weak electron-accepting nature of the 2, 1, 3-thiadiazole ring as a substituent of two ortho hydrogen atoms in the benzene ring.

The opinion put forward on the nature of the shift in the electron cloud in benzo-2, 1, 3-thiadiazole and its selena analog (I) does not contradict the results of structural investigations [3, 4, 48], according to which compounds I and III are symmetrical relative to the plane passing through the sulfur (or selenium) atom and perpendicular to the plane of the molecule. So far as concerns the distribution of the electron density in the thiadiazole ring, experimental data are in agreement with the hypothesis of a shift in the electron cloud in the direction of the nitrogen with the formation of the mesomeric ion Ib with onium sulfur (or selenium). Thus, for example, benzo-2, 1, 3-selenadiazole is a stronger base than its thia analog; it forms salts more readily, and these are more stable [52]; it is alkylated at the nitrogen atom more readily, and the corresponding quaternary salts are more stable [61, 62]. It is possible to arrive at the assumption that I is capable of reacting in the form of the bipolar compound Ib by considering its possible limiting structures.



I Ib

Of the six limiting structures, the most favorable energetically are I and Ib.



I Ia Ib

REFERENCES

1. V. G. Pesin and V. A. Sergeev, KhGS [Chemistry of Heterocyclic Compounds], 5, 65, 1969.

2. O. Hinsberg, Ber., 22, 2889, 1889.

3. V. Luzzati, Acta cryst., 4, 193, 1951.

4. A. I. Kitaigorodskii, Organic Crystallography [in Russian], Izd-vo AN SSSR, Moscow, 1955.

5. L. S. Efros and R. M. Levit, ZhOKh, 25, 199, 1955.

6. L. S. Efros and Z. V. Todres-Selektor, ZhOKh, 27, 983, 1957.

7. L. S. Efros and Z. V. Todres-Selektor, ZhOKh, 27, 3127, 1957.

8. L. S. Efros and A. V. El'tsov, ZhOKh, 28, 2172, 1958.

9. V. L. Pozdyshev, Z. V. Todres-Selektor, and L. S. Efros, ZhOKh, 30, 2551, 1960.

10. L. S. Efros, R. P. Polyakova, and M. G. Argiti, ZhOKh, 32, 516, 1962.

11. L. S. Efros, Usp. khim., 29, 181, 1960.

12. V. G. Pesin, A. M. Khaletskii, and I. A. Lotsmanenko, ZhOKh, 33, 1746, 1963.

13. V. G. Pesin and I. A. Belenkaya-Lotsmanenko, KhGS [Chemistry of Heterocyclic Compounds], 3, 666, 1967.

14. V. G. Pesin, I. A. Belenkaya-Lotsmanenko, and A. M. Khaletskii, ZhOKh, 34, 3763, 1964.

15. Chao Chih-chung, Thesis [in Russian], Leningrad Chemical and Pharmaceutical Institute, 1956.

16. L. Weinstock, Diss. Abstr., 19, 3136, 1959.

17. D. Shew, Diss. Abstr., 20, 1593, 1959.

18. V. G. Pesin, V. A. Sergeev, and A. M. Khaletskii, ZhOKh, 34, 261, 1964.

19. V. G. Pesin, A. M. Khaletskii, and V. A. Sergeev, ZhOKh, 32, 181, 1962.

20. N. Donaldson, The Chemistry and Technology of Ethylene Compounds [Russian translation], GKhI, Moscow, 1963.

21. E. Animal, D. Dal Monte, and E. Sandri, Boll. sci. fac. chim. ind. Bologna, 22, 48, 1964.

22. I. A. Belenkaya-Lotsmanenko and V. G. Pesin, Subjects of a Scientific Conference at the Leningrad Chemical and Pharmaceutical Institue [in Russian], Leningrad, 1966.

23. M. P. Gava, R. H. Schlessinger, Tetrah. Lett., 50, 3815, 1964.

24. K. Takeda, K. Kitahonoki, M. Sugiura, V. Takano, Ber., 95, 2344, 1962.

25. S. A. D'yachenko, Thesis [in Russian], Leningrad Chemical and Pharmaceutical Institute, Leningrad, 1967.

26. I. V. Machinskaya and V. A. Barkhash, Reactions and Methods of Investigation of Organic Compounds, Vol. 9 [in Russian], GNTIKhL, Moscow, 1959.

27. A. P. Terent'ev and L. A. Yanovskaya, Reactions and Methods of Investigation of Organic Compounds, Vol. 6 [in Russian], GNTIKhL, Moscow, 1957.

28. V. S. Korobkov, I. V. Kuzin, L. A. Kaukhova, V. G. Pesin, and A. M. Khaletskii, Spectroscopy: Methods and Applications [in Russian], Nauka, Moscow, p. 130, 1964.

29. V. S. Korobkov, V. G. Pesin, L. P. Zubanova, and V. A. Sergeev, The Use of Molecular Spectroscopy in Chemistry [in Russian], Nauka, Moscow, p. 57, 1966.

30. S. G. Fridman, ZhOKh, 31, 1096, 1961.

31. S. G. Fridman and L. I. Kotova, ZhOKh, 32, 2871, 1962.

32. S. G. Fridman, ZhOKh, 30, 1685, 1960.

33. V. G. Pesin, A. M. Khaletskii, and E. K. D'yachenko, ZhOKh, 32, 3505, 1962.

34. Organic Syntheses [Russian translation], IL, Moscow, 4, 426, 1953.

35. S. Gabriel and A. Sonn, Ber., 40, 4850, 1907.

36. H. C. Longuet-Higgins, Trans. Faraday Soc., 45, 173, 1949.

37. L. Pauling and V. Schomaker, J. Am. Chem. Soc., 61, 1769, 1939.

38. G. Cilento, Chem. Rev., 60, 1, 47, 1960.

39. H. Erlenmeyer and M. Leo, Helv. Chim. Acta, 15, 1180, 1932; 16, 733, 897, 1381, 1933.

40. G. Milazzo, Experientia, 3, 370, 1947.

41. J. Godart, J. Chim. Phys., 34, 70, 1947.

42. M. R. Padhye and S. R. Desai, Trans. Faraday Soc., 49, 1386, 1953.

43. H. Erlenmeyer, E. H. Schmid, and A. Kleiber, Helv. Chim. Acta, 25, 375, 1942.

44. R. Zahradnik and J. Coutecky, Coll., 26, 156, 1961.

45. R. Y. Wen, Diss. Abstr., 23, 4121, 1963.

46. F. H. Marquardt, Diss. Abstr., 21, 3272, 1961.

47. J. M. Gill, Diss. Abstr., 24, 2690, 1964.

48. R. R. McDonald, Diss. Abstr., 23, 1897, 1962.

49. F. A. Momany and R. A. Bonham, J. Am. Chem. Soc., 86, 162, 1964.

50. V. Dobyns and L. Pierce, J. Am. Chem. Soc., 85, 3553, 1963.

51. L. Pauling, Nature of the Chemical Bond and the Structure of Molecules and Crystals [Russian translation], Goskhimizdat, Moscow-Liningrad, 1947.

52. V. A. Sergeev, Thesis [in Russian], Leningrad Chemical and Pharmaceutical Institute, Leningrad, 1965.

53. E. K. D'yachenko, Thesis [in Russian], Leningrad Chemical and Pharmaceutical Institute, 1966.

54. V. G. Pesin and I. A. Belenkaya, KhGS [Chemistry of Heterocyclic Compounds], 3, 289, 1967.

55. V. Sherman, Heterocyclic Compounds, Vol. 7 [Russian translation], Mir, Moscow, 1965.

56. E. R. Ward, W. H. Poesche, D. Higgins, and D. D. Heard, J. Chem. Soc., 2374, 1962.

57. R. S. Karlinskaya and N. V. Khromov-Borisov, ZhOKh, 32, 1847, 1962.

58. R. W. Hill and L. E. Sutton, J. Chim. Phys., 46, 244, 1949; C. A. 44, 8714, 1950.

59. O. A. Reutov, Theoretical Principles of Organic Chemistry [in Russian], MGU, 1964.

60. O. A. Osipov, V. I. Minkin, and Yu. B. Kletenik, Handbook of Dipole Moments [in Russian], Vysshaya shkola, Moscow, 1965.

61. A. I. Nunn and I. T. Ralph, J. Chem. Soc., 6769, 1965.

62. A. I. Nunn and I. T. Ralph, J. Chem. Soc., 1568, 1966.

63. W. Baker and W. D. Ollis, Quart. Rev., 11, 15, 1957.

64. V. G. Pesin, A. M. Khaletskii, Chao Chih-chung, ZhOKh, 27, 1575, 1957; DAN, 113, 627, 1957.

65. V. G. Pesin, A. M. Khaletskii, and Chou Ch'in, ZhOKh, 28, 2089, 1958; DAN, 114, 811, 1957.

66. V. G. Pesin and R. S. Muravik, Izv. AN Latv. SSR, 6, 725, 1964.

67. V. G. Pesin and E. K. D'yachenko, KhGS [Chemistry of Heterocyclic Compounds], 3, 97, 1967.

68. V. G. Pesin, Thesis [in Russian], LKhFI, Leningrad, 1967.

69. C. Brizzi, D. Dal Monte, and E. Sandri, Ann. Chim., 54, 476, 1964.

70. V. V. Plemenkov, Thesis [in Russian], Author's abstract, Kazan State University, 1967.

71. G. Collins, Diss. Abstr., 27 (2), 403, 1966.

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