Table II. Mulliken Population Analyses

	Center population				Bond orders				
Point no.	C	H_E[a]	H_L[b]	H_{NR}[c]	CH_L[b]	CH_E[a]	CH_{NR}[c]	d_1[d]	d_2[e]
∞	6.54	2.00	0.869	0.869	0.387	0.00	0.387	2.06	∞
14	6.36	1.904	1.187	0.853	0.254	−0.05	0.411	2.60	4.00
21	6.27	1.818	1.359	0.852	0.184	−0.006	0.417	2.90	3.70
26	6.24	1.773	1.422	0.851	0.161	0.008	0.418	3.00	3.60
32	6.23	1.730	1.484	0.851	0.137	0.035	0.419	3.10	3.50
39	6.22	1.691	1.532	0.852	0.115	0.055	0.420	3.20	3.40
45	6.22	1.613	1.613	0.852	0.086	0.086	0.420	3.30	3.30

[a] H_E is the entering hydrogen, *i.e.*, the hydrogen farthest from the carbon. [b] H_L is the leaving hydrogen, *i.e.*, the hydrogen along the H_E–C bond extension. [c] H_{NR} refers to the nonreacting hydrogens. [d] The distance between C and H_L is d_1. [e] The distance between C and H_E is d_2.

with the symmetry of the vibration carrying CH_5^- into $CH_4 + H^-$.

Assuming that we have explored the path corresponding to an SN2 reaction, it is interesting to note the population analyses in Table II. The interesting feature is that the electron densities on both carbon and the nonreacting hydrogens decrease on going from methane to the saddle point. This rather surprising result appears to be consistent with the experimental observation that electron donating substituents on carbon increase the rates of SN2 reactions.[6]

Quite recently, Berthier[7] has reported *ab initio* LCGO-MO-SCF calculations pertaining to the SN2 reaction of F^- with CH_3F. Only the two regions corresponding to reactants and D_{3h} species were examined closely. In agreement with the present study, it was found that the electron densities on carbon and on the hydrogens decrease on going from reactants to "transition state." The density on carbon decreased by 0.123 unit, and the densities on each of the hydrogens decreased by 0.008 unit. In the present study, the corresponding decreases are 0.32 and 0.017 unit, respectively.

In contrast to the present results, Berthier finds the $CH_3F_2^-$ transition state to be 8.8 kcal/mol more stable than the separated reactants. It should be recalled that the same situation was encountered in our earlier work[2] on the reactions of H^- and F^- with hydrogen molecules. The H^- reaction showed a transition state less stable than separated reactants, while the F^- reaction gave the opposite result. We are still unable to understand the origin of these unusual results, but note that positive "excitation energies" have been found for ion–molecule reactions only in the cases where hydride ion is both the entering and leaving group.

Acknowledgments. We are grateful to the Computer Center, State University of New York at Buffalo, for the donation of massive amounts of computer time.

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(6) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 3 ff; C. K. Ingold, *Quart. Rev.* (London), **11**, 1 (1957).

(7) G. Berthier, D. J. David, and A. Viellard, *Theor. Chim. Acta*, **14**, 329 (1969).

A Semiempirical Description of the Diamagnetic Susceptibilities of Aromatic Molecules

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Abstract: A semiempirical description of the diamagnetic susceptibilities of conjugated organic molecules has been derived. The susceptibility is represented as a sum of three terms, namely the contributions from the σ electrons and from the π electrons and the contribution from σ–π interactions. The π-electron contribution is derived from London's theory and the other terms are expressed in terms of atomic susceptibilities, bond susceptibilities, and bond–bond interactions. As an example the polyacenes are discussed, where satisfactory agreement with experiment is obtained.

In previous work[2] the authors have put forward a semiempirical theory of the diamagnetic susceptibilities of saturated organic molecules. The present paper extends this theory to conjugated molecules.

It should be noted that in deriving the theory for saturated molecules we made a few assumptions which are not valid in the case of conjugated systems and it is therefore necessary to reconsider the theoretical derivation. The first assumption was that the molecular eigenfunctions of the ground and excited states may be approximated as single-determinant LCAO–MO functions. The second assumption was that the

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(1) Supported by the National Science Foundation Undergraduate Participation Program.

(2) (a) H. F. Hameka, *J. Chem. Phys.*, **34**, 1996 (1961); (b) P. S. O'Sullivan and H. F. Hameka, *J. Amer. Chem. Soc.*, **92**, 25 (1970).

molecular orbitals are localized in the various bonds or on the atoms, and the third assumption was that the bond orbitals are basically independent of the location of the bond and may be treated as typical of the type of bond. Obviously, the second and third assumptions are no longer true in the case of conjugated molecule.

Let us consider a planar, conjugated, molecule, so that each molecular orbital is either symmetric with respect to the molecular plane or antisymmetric. The former type is called a σ orbital and the latter type a π orbital. It has been derived previously[3] that the diamagnetic susceptibility of a molecule with a closed shell ground state is obtained as

$$\chi = 2\chi_0 \sum_{k=1}^{N} \left[\frac{G_{kk} - \Delta_{kk}\epsilon_k}{\Delta_{kk}} - \sum_{1 \neq k}^{N} \frac{\Delta_{kl}(G_{lk} - \Delta_{lk}\epsilon_k)}{\Delta_{kk}\Delta_{ll}} - \sum_{n=n+1}^{\infty} \frac{(G_{nk} - \Delta_{nk}\epsilon_k)(G_{nk} - \Delta_{nk}\epsilon_k)^*}{\Delta_{kk}\Delta_{nn}(\epsilon_n - \epsilon_k)} \right] \quad (1)$$

Here it has been assumed that the molecular ground state eigenfunction ψ_0 is approximated as a single determinant, constructed from molecular orbitals ϕ_k. Subscripts k and l have been used for the N filled molecular orbitals and the subscript n denotes empty molecular orbitals. The matrix elements in eq 1 are defined as

$$\begin{aligned} G_{lk} &= \langle \tilde{\phi}_l | G_{l\mathrm{op}} | \tilde{\phi}_k \rangle \\ \Delta_{lk} &= \langle \tilde{\phi}_l | \tilde{\phi}_k \rangle \end{aligned} \quad (2)$$

where the $\tilde{\phi}_k$'s are obtained from the ϕ_k by introducing gauge invariant atomic orbitals and G_{op} is an effective one-electron Hamiltonian in the presence of a magnetic field.[3]

Let us now adapt eq 1 to a conjugated organic molecule by separating the molecular orbitals into the σ- and π-type molecular orbitals

$$\chi = 2\chi_0(\chi_\Sigma + \chi_\Pi - \chi_{\Sigma\Pi}) \quad (3)$$

Let us now attempt to express the various quantities in eq 3 in terms of molecular parameters. We consider the aromatic hydrocarbons only.

The first term, χ_Σ, is similar to the susceptibility of an alkane molecule which we considered previously.[2a] By analogy with the saturated molecules it is written as

$$\chi_\Sigma = N_{\mathrm{C}}\chi_{\mathrm{C}}^1 + N_{\mathrm{CH}}\chi_{\mathrm{CH}} + N_\sigma\chi_\sigma - N_{\sigma,\sigma}\chi_{\sigma,\sigma} - N_{\sigma,\mathrm{CH}}\chi_{\sigma,\mathrm{CH}} - N_{\mathrm{CH,CH}}\chi_{\mathrm{CH,CH}} \quad (4)$$

Here N_{C} is the number of carbon atoms, N_{CH} the number of CH bonds, N_σ the number of C–C σ bonds, $N_{\sigma,\sigma}$ the number of pairs of adjacent C–C σ bonds, etc. The parameter χ_{C}^1 represents the susceptibility of a ls electron on a carbon, χ_{CH} the susceptibility of a CH bond, and χ_σ the susceptibility of a C–C σ bond. The other parameters are second-order contributions to the susceptibility, which may be looked upon as bond–bond interactions.

The second term of eq 3, χ_Π, is identical with the susceptibility contribution that was considered by London[4] in order to account for the anisotropy in the susceptibility. London calculated this contribution for a small number of polyacenes. It was shown[4] that for an arbitrary polyacene χ_Π may be expressed in terms of χ_Π for benzene by means of simple MO theory. Hence the terms χ_Π for all polyacenes may be expressed in terms of a single parameter, $\chi_{\Pi,\mathrm{b}}$. The values of χ_Π, expressed in terms of $\chi_{\Pi,\mathrm{b}}$, have been evaluated for a large number of aromatic compounds by Pullman and Pullman,[5] and these results will be used in the subsequent discussion.

Let us finally consider the term $\chi_{\Sigma\Pi}$. If we substitute for the molecular orbitals their linear combinations

$$\phi_{k'} = \sum_j C_{k',j}\pi_j \quad (5)$$

then $\chi_{\Sigma\Pi}$ may be expressed as

$$\chi_{\Sigma\Pi} = \sum_{l'} \sum_j C_{l',j}C_{l',j}^*[\chi_{j,\mathrm{CH}}' + 2\chi_{j.\sigma}'] + \sum_{n'} \sum_j C_{n'j}'C_{n'j}^*[\chi_{j,\mathrm{CH}}^2 + 2\chi_{j,\sigma}^2] + \sum_{k'=1}^{N'} \sum_j C_{k',j}C_{k',j}^*[\chi_{j,\mathrm{CH}}^3 + 2\chi_{j,\sigma}^3] \quad (6)$$

Here the first and last summations are to be performed over the filled π molecular orbitals and the second summation is to be taken over the empty π orbitals. We have

$$\begin{aligned} \sum_{l'} C_{l',j}C_{l',j}^* &= \sum_{k'} C_{k',j}C_{k',j}^* = {}^1\!/_2\rho_j \\ \sum_{n'} C_{n',j}C_{n',j}C_{n'.j}^* &= 1 - {}^1\!/_2\rho_j \end{aligned} \quad (7)$$

where ρ_j is the π electron charge density on site j. Hence

$$\chi_{\Sigma\Pi} = \sum_j \rho_j[{}^1\!/_2(\chi_{j,\mathrm{CH}}^1 - \chi_{j,\mathrm{CH}}^2 + \chi_{j,\mathrm{CH}}^3) + (\chi_{j,\sigma}^1 - \chi_{j,\sigma}^2 + \chi_{j,\sigma}^3)] + {}^1\!/_2 N_\Pi[\chi_{j,\mathrm{CH}}^2 + 2\chi_{j,\sigma}^2] \quad (8)$$

where N_Π is the number of carbon atoms. By introducing new parameters this may be rewritten as

$$\chi_{\Sigma\Pi} = N_\pi[\chi_{j,\mathrm{CH}} + 2\chi_{j,\sigma}] + \sum_j \rho_j(\chi_{j,\mathrm{CH}}' + 2\chi_{j,\sigma}') \quad (9)$$

Here $\chi_{j,\mathrm{CH}}$ and $\chi_{j,\mathrm{CH}}'$ are susceptibility contributions due to the interaction between an atomic π orbital and an adjacent CH bond and $\chi_{j,\sigma}$ and $\chi_{j,\sigma}'$ represent the interaction between an atomic π orbital and an adjacent C–C σ bond.

Polyacenes

We wish to apply the theoretical results of the previous sections to the description of the diamagnetic susceptibilities of the polyacenes. In this case it is possible to make some further simplifications. According to eq 3, 4, and 9 we may represent the susceptibility of a polyacene molecule as

$$\chi = N_{\mathrm{C}}\chi_{\mathrm{C}}^1 + N_{\mathrm{CH}}\chi_{\mathrm{CH}} + N_\sigma\chi_\sigma - N_{\sigma,\sigma}\chi_{\sigma,\sigma} - N_{\sigma,\mathrm{CH}}\chi_{\sigma,\mathrm{CH}} - N_{\mathrm{CH,CH}}\chi_{\mathrm{CH.CH}} + N_\Pi[\chi_{j,\mathrm{CH}} + 2\chi_{j,\sigma}] + \sum_j \rho_j(\chi_{j,\mathrm{CH}}' + 2\chi_{j,\mathrm{CH}}') + K\chi_{\Pi,\mathrm{b}} \quad (10)$$

where K is the London parameter,[4] for which we will take the value reported by Pullman and Pullman.[5]

In the case of a polyacene molecule all the parameters ρ_j are equal to unity and the parameters $\chi_{j,\mathrm{CH}}$, $\chi_{j,\sigma}$, $\chi_{j,\mathrm{CH}}'$, and $\chi_{j,\sigma}'$ are independent of j. This means that the susceptibility may be written in the form

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(3) H. F. Hameka, *Physica*, **28**, 908 (1962).

(4) F. London, *J. Phys. Radium*, **8**, 397 (1937).

(5) B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique," Masson et Cie, Paris, 1952, p 545.

$$\chi = N_C\chi_C + N_{CH}\chi_{CH} + N_\sigma\chi_\sigma - N_{\sigma,\sigma}\chi_{\sigma,\sigma} - N_{\sigma,CH}\chi_{\sigma,CH} - N_{\pi,CH}\chi_{\pi,CH} - N_{\pi,\sigma}\chi_{\pi,\sigma} + K\chi_{\Pi,b} \quad (11)$$

As an example the susceptibilities χ_b of benzene and χ_n of naphthalene are written according to eq 11 and it is found that these susceptibilities may be expressed in terms of the parameters

$$A = 6\chi_C + 6\chi_\sigma + 6\chi_{CH} - 6\chi_{\sigma,\sigma} - 12\chi_{\sigma,CH} - 6\chi_{\pi,CH} - 12\chi_{\pi\sigma}$$

$$B = 4\chi_C + 5\chi_\sigma + 2\chi_{CH} - 8\chi_{\sigma,\sigma} - 4\chi_{\sigma,CH} - 2\chi_{\pi,CH} - 10\chi_{\pi,\sigma} \quad (12)$$

$$D = \chi_{\Pi,b}$$

The result is

$$\chi_b = A + K_bD$$
$$\chi_n = A + B + K_nD \quad (13)$$

Let us now compare the susceptibility expressions for anthracene, phenanthrene, and pyrene; they will be denoted by χ_a, χ_p, and χ_{py}, respectively. It is easily seen that

$$\chi_a = A + 2B + K_aD$$
$$\chi_p = A + 2B + K_pD \quad (14)$$

In order to represent χ_{py} we introduce a new parameter C, which is defined as

$$C = \chi_C + \chi_\sigma + \chi_{\sigma,\sigma} - 2\chi_{\sigma,CH} - \chi_{\pi,CH} - 2\chi_{\pi,\sigma} \quad (15)$$

This enables us to write χ_{py} as

$$\chi_{py} = A + 3B - 2C + K_{py}D \quad (16)$$

The representation in parameter form of the susceptibilities of the polyacenes is quite straightforward. Apart from the term containing the parameter D, it may be seen that the susceptibility of benzene is given by the parameter A. The addition of another benzene ring to the polyacene system is given by the parameter B if the new ring has one side in common with the system, by the parameter $(B - C)$ if it has two sides in common, by $(B - 2C)$ if it has three sides in common, etc.

Calculations

It was found that the experimental susceptibilities and the π-electron contributions to the susceptibilities are available for the ten compounds that we have listed in Table I. The best values of the four parameters were determined by means of the least-squares method. One compound, chrysene, shows a large discrepancy and this result was excluded from determination of the parameters. The agreement between the experimental values and the predicted susceptibilities for the remaining nine molecules is much better than expected and it may be fortuitous. There is no ready explanation for the large deviations in the case of chrysene other than the speculation that the experimental value may be inaccurate.

The best agreement between theory and experiment is obtained for the following set of parameters: $A = 43.8286$, $B = 23.4107$, $C = 8.6421$, $D = 11.3003$, expressed in terms of -10^6 cgs units. It is interesting to note that the value of D that is obtained here is much smaller than the result obtained by London.[4] However, the D value of 11.3 is in good agreement with the value $D = (31.2/3) = 10.4$ that was derived by means of the SCF calculation by Hall and Hardisson.[6]

Table I. The Molar Diamagnetic Susceptibilities of the Polyacenes

Compound		χ_{th}	χ_{exp}	Ref
Benzene	$A + D$	55.129	54.85	*a*
Naphthalene	$A + B + 2.185D$	91.930	91.9	*b*
Anthracene	$A + 2B + 3.448D$	129.613	129.4	*b*
Phenanthrene	$A + 2B + 3.246D$	127.331	127.9	*b*
Pyrene	$A + 3B - 2C + 4.580D$	148.532	147.9	*b*
Naphthacene	$A + 3B + 4.747D$	167.703	168.0	*c*
Chrysene	$A + 3B + 3.806D$	157.070[d]	166.67	*c*
Pentacene	$A + 4B + 6.062D$	205.974	205.4	*c*
Perylene	$A + 4B - 2C + 4.118D$	166.722	166.8	*b*
Coronene	$A + 6B - 6C + 9.794D$[e]	243.115	243.3	*c*

[a] W. R. Angus and W. K. Hill, *Trans. Faraday Soc.*, **39**, 190 (1943). [b] H. Akamatu and Y. Matsunaga, *Bull. Chem. Soc. Jap.*, **26**, 364 (1953). [c] H. Akamatu and Y. Matsunaga, *ibid.*, **29**, 800 (1956). [d] This value was excluded in fitting the parameters because of the large difference. [e] The coefficients of the parameters D were taken from ref 5.

The parameter D represents a susceptibility contribution that is perpendicular to the plane of the molecule and in the past it was customary to consider it as the main contribution to the anisotropy in the diamagnetic susceptibility. Recent work by Amos and Roberts[7] indicates that this is not quite true because a sizable part of the anisotropy should be attributed to anisotropies in the other parameters. In order to investigate this question the present semiempirical treatment was extended to the susceptibilities that are perpendicular to the plane for those molecules where the experimental values are reported by Amos and Roberts.[7] Each of the parameters may be represented as

$$A = {}^1/_3(A_x + A_y + A_z) \quad (17)$$

where the z axis is taken perpendicular to the plane. It is noted that $D_x = D_y = 0$, $D_z = 3D$, and $A^* = A_z$, $B^* = B_z$, and $C^* = C_z$ are defined. The calculation is reported in Table II and the parameter values are $A^* = 60.2028$, $B^* = 35.7164$, $C^* = 3.5591$. It should be noted that the contributions of A and B to $\chi_\perp$ are larger than the contributions to $\chi_\parallel$ so that the anisot-

Table II. Molar Susceptibilities Perpendicular to the Plane of the Molecule

Compound		χ_{th}	χ_{exp}	Ref
Benzene	$A^* + D$	94.104	94.6	*a*
Naphthalene	$A^* + B^* + 2.185D$	169.993	169.0	*b*
Anthracene	$A^* + 2B^* + 3.448D$	248.526	250.7	*c*
Phenanthrene	$A^* + 2B^* + 3.246D$	241.678	240.0	*d*
Pyrene	$A^* + 3B^* - 2C^* + 4.580D$	315.500	315.5	*e*

[a] J. Horau, N. Lumboroso, and A. Pacault, *C. R. Acad. Sci., Paris*, **242**, 1702 (1956). [b] J. Hoarau, *Ann. Chim.* (Paris), **1**, 544 (1956). [c] M. Leela, Ph.D. Thesis, University of London, 1958. [d] K. S. Krishnan and S. Bannerjee, *Phil. Trans. Roy. Soc. London*, *Ser. A*, **234**, 265 (1935). [e] D. W. Davies, *Nature*, **190**, 1102 (1961).

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(6) G. G. Hall and A. Hardisson, *Proc. Roy. Soc.*, *Ser. A*, **268**, 328 (1962), as quoted by A. T. Amos and H. G. F. Roberts, *J. Chem. Phys.*, **50**, 2375 (1969).

(7) A. T. Amos and H. G. F. Roberts, *ibid.*, **50**, 2375 (1969).

ropies in the susceptibilities are caused just as much by anisotropies in the parameters A and B as by the presence of the parameter D. This conclusion agrees with the results of Amos and Roberts.[7] It should be noted, however, that the results of Table II are not as meaningful as the results of Table I. In Table II three parameters are adjusted to represent five experimental results that do not seem very accurate, and the authors feel that the number of experimental values is not sufficiently large for producing a meaningful theoretical description.

Discussion

The idea of deriving a semiempirical description of the diamagnetic susceptibilities of organic molecules is not a new one and the literature on this subject is fairly extensive. Papers by London,[4] Hall and Hardisson,[6] Amos and Roberts,[7] and Gawer and Dailey,[8] are all concerned in particular with aromatic molecules. However, it is felt that the present investigation contains some features that are not contained in the previous theoretical descriptions. The work by London[4] is concerned only with the π electrons and it is fairly well established now that the σ electrons contribute significantly to both the total susceptibilities and to the anisotropies. The other authors who are quoted above attempt to derive semiempirical descriptions of the susceptibilities of aromatics and they all include the σ electrons in their considerations. The main difference between these theories and the present one is that they attempt to express the contributions of the σ electrons in terms of atomic contributions while we express them in terms of the contributions of the localized bonds and of the bond-bond interactions. The authors feel that this representation has the advantage that it can be justified in a more or less rigorous theoretical fashion and, also, that it is more precise than any of the other methods. It should be noted that London's calculation[4] is perhaps less accurate than Hall and Hardisson's, but the present approach uses only the ratios of London's results and it is felt that these ratios are quite accurate.

The results of this paper show how this semiempirical description of diamagnetic susceptibilities[2b] may be extended to conjugated systems. The polyacenes have been treated, as an example, but the formalism developed here is suitable for the description of all types of conjugated molecules. It was shown that in the case of a conjugated molecule, having delocalized molecular orbitals, the diamagnetic susceptibility may be represented as a sum of three parts, χ_Σ, χ_Π, $\chi_{\Sigma\Pi}$. These parts are the contributions of the σ electrons and of the π electrons and a contribution due to σ–π interactions. The parts χ_Σ and $\chi_{\Sigma\Pi}$ are treated in the same fashion as in the authors' theory of saturated molecules. The part χ_Π is derived from London's theory.[4,5] Even though the absolute values of London's theory[4,5] may not be too accurate it is felt that the ratio of these results for different molecules are quite reliable. The satisfactory agreement between our semiempirical susceptibility values and the experimental results seem to support this assumption.

Finally, the authors feel that a combination of the methods described above with the procedures discussed previously[2] constitutes the framework for a general semiempirical description of the diamagnetic susceptibilities of all organic molecules, both saturated and unsaturated.

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[8] A. H. Gawer and B. P. Dailey, *J. Chem. Phys.*, **42**, 2658 (1965).

Mercury ($^3P_1$) Sensitized Photolysis of 2,5-Dimethylfuran

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Abstract: The photodecomposition of 2,5-dimethylfuran vapor sensitized by mercury ($^3P_1$) atoms was a complex process in which more than 11 products were formed in characterizable amounts. This number did not include dimeric and condensed materials. The products, in the order of decreasing abundance, were 4-methylcyclopent-2-enone, *cis*- and *trans*-1,3-pentadienes, CO, 1-methyl-3-acetylcyclopropene, hexa-3,4-dien-2-one, 2-ethyl-5-methylfuran, isoprene, 1,3-dimethylcyclopropene, 2-pentyne, and propylene. The formation of 2-ethyl-5-methylfuran was the only process that was totally eliminated on the addition of oxygen. It is hence believed to be the only reaction of free-radical origin. The three minor C_5H_8 products were shown to be formed by the secondary photolysis of the 1,3-pentadienes. The intermediate that leads to 4-methylcyclopent-2-enone and (CO + 1,3-pentadiene) is best rationalized as a carbene while the intermediate that gives the two other isomeric ketones may be a 1,3-diradical. Quantum yields and data on pressure quenching have also been obtained.

In earlier studies on the mercury-photosensitized decomposition of furan[2] and methylfurans[3,4] the most important process was postulated to be a ring contraction to give cyclopropene-3-carboxaldehyde (I). Ullman and Singh[5] had first observed such a

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[1] Postdoctoral Fellow, 1968–1970.

[2] R. Srinivasan, *J. Amer. Chem. Soc.*, **89**, 1758, 4812 (1967); *Pure Appl. Chem.*, **16**, 65 (1968).

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