Tetrahedron. Vol. 29, pp. 2009 to 2014. Pergamon Press 1973. Printed in Great Britain

THE NATURE OF SULFUR BONDING IN THIOPYRYLIUM CATION

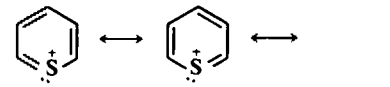
S. YONEDA, T. SUGIMOTO and Z. YOSHIDA*

Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto 606, Japan

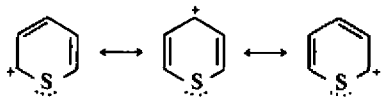
(*Received in Japan* 20 *January* 1973; *Received in UK for publication* 28 *February* 1973)

Abstract – Comparison of the PMR spectrum of thiopyrylium cation with those of the oxygen (pyrylium cation) and nitrogen (pyridinium cation) analogs has suggested the unique electronic structure of the thiopyrylium cation. To investigate this structure the extended Hückel MO calculations have been carried out using two basis sets, one with and another without sulfur 3d orbitals. The electronic structure of thiopyrylium cation can be rationalized by the 3d orbital involvement of the S atom in the basis set. The primary effect of the involvement of 3d orbitals on the S atom is shown to be the electron transfer from the ring carbon fragment, in particular from the β ring carbons, to the S atom, with an accompanying increase in sulfur-α-carbon bond order.

The structure of the thiopyrylium cation is of interest in concern with the nature of S-bonding. The ground state structure of this ion is commonly shown as the following resonance hybrids (**1–5**).

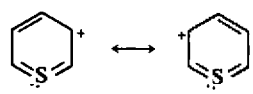


1 **2**



3 **4** **5**

However, it should be considered that the resonance hybrids **6**, **7** utilizing the sulfur 3d orbitals besides the above (3p-2p)π bonding forms (**1**, **2**) might contribute to some extent to the ground state structure.



6 **7**

Although the 3d orbital participation on the S atom in the thiopyrylium cation has briefly and qualitatively been discussed,[1] no attempt has, so far, been made to investigate this problem in detail. Very recently, Palmer and Findlay have discussed whether 3d orbitals on a S atom play an important role in the bonding scheme of thiopyrylium cation using the procedure of a linear combination of gaussian orbitals, and concluded that the 3d orbitals are used only to a trivial extent.[2] However, the 3d orbital participation seems to be partly or wholly responsible for the electronic structure of the thiopyrylium cation, because of the striking difference between the thermal stabilities of the thiopyrylium cation and its oxygen analog i.e. pyrylium cation.[3–6] These situations prompted us to present our investigation on the electronic structure of the thiopyrylium cation by the PMR spectra and the extended Hückel MO method using two basis sets, one with and another without S 3d orbitals.

*To whom correspondence should be addressed.

EXPERIMENTAL

Spectra. IR spectra were recorded on a Hitachi grating IR spectrophotometer Model-215; ultraviolet spectra on a Hitachi EPS-3T recording photometer using acetonitrile as solvent; PMR spectra in trifluoroacetic acid on a Varian T-60 spectrometer.

Thiopyrylium perchlorate. The compound was prepared[7] and purified by reprecipitation from acetonitrile–ether: IR (KBr) 1160–1000 cm^{-1} (ClO_4^-); UV (CH_3CN) λ_{max} 246 and 285 nm; NMR (CF_3COOH) δ 10·20 (2H, α-protons) and 9·11 (3H, β- and γ-protons).

Pyrylium perchlorate. The compound was also prepared[7] and purified by reprecipitation from acetonitrile–ether: IR (KBr) 1160–1000 cm^{-1} (ClO_4^-); UV (CH_3CN) λ_{max} 219 and 270 nm, NMR (CF_3COOH) δ 9·70 (2H, α-protons), 9·36 (1H, γ-proton) and 8·53 (2H, β-protons).

N-Ethylpyridinium perchlorate. The compound was prepared using a procedure of Menschutkin:[8] m.p. 72·5–73·0°; IR (KBr) 1160–1000 cm^{-1} (ClO_4^-); UV (CH_3CN) λ_{max} 259 nm; NMR (CF_3COOH) δ 8·81 (2H, α-protons), 8·60 (1H, γ-proton), 8·22 (2H, β-protons), 4·82 (2H, methylene protons) and 1·81 (3H, methyl protons).

Calculation details. The extended Hückel MO calculations were carried out in the usual manner.[9] The diagonal elements of the Hamiltonian matrix (H_{ii}) were approximated by the atomic valence state ionization potentials. In the present calculations they have been obtained from the tables of Hinze and Jaffé,[10] and the 3d orbital of the S atom from the work of Cusachs and Linn.[11] The off-

diagonal Hamiltonian matrix elements (H_{ij}) were calculated by using the Wolfsberg-Helmholtz approximation:[12]

$$H_{ij} = 0{\cdot}5K(H_{ii} + H_{jj})S_{ij}$$

where S_{ij} is the overlap integral between the ith and jth atomic orbitals. K is evaluated as 1·75 by Hoffmann. The overlap integrals are calculated from the Cartesian coordinates of the atoms and the orbital exponents of the single Slater functions in a similar manner to that described by Mulliken.[13] The orbital exponents were taken from the Slater's rule, except for the H1s and S3d orbitals, for which we used 1·2 and 0·983, respectively. The value of 1·2 for the exponent in the H1s orbital was taken from SCF MO calculations.[14] The various values of the Slater exponent for the 3d orbitals have been discussed and applied to some calculations.[15-20] It has been previously recognized that the shape of a 3d orbital and consequently its Slater exponent is sensitive to its molecular environment.[21] Therefore, the orbital exponent should be optimized to suit the molecular environment. Values of the exponents for Slater d orbitals have been obtained by minimizing the total energy of each molecule with respect to these exponents.[22] This method has been used in the present work. The total energy was calculated with varying values of the exponent for sulfur 3d orbital. The results are shown in Fig 1. An energy minimum appears at an exponent value of 0·983. This value was used in the subsequent calculations. A geometry of the thiopyrylium cation was assumed to have C_{2v} symmetry (Fig 2). We took in the present calculation an appreciably short C–S distance of 1·70 Å chosen in the SCF MO calculation.[23] All C–C bond distances were taken as 1·40 Å, and the C–H bond distances as 1·10 Å.

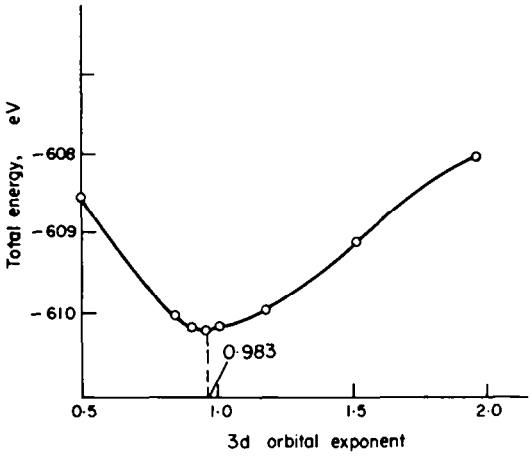


Fig 1. Total energy as a function of sulfur 3d exponent.

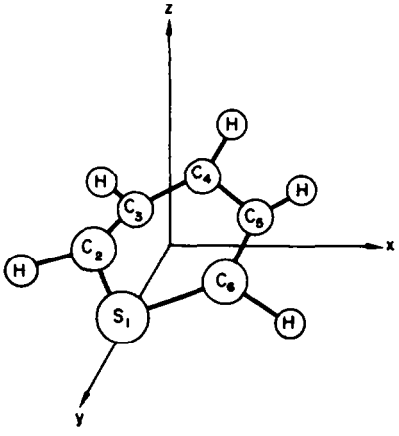


Fig 2. Assumed geometry of the thiopyrylium cation.

RESULTS AND DISCUSSION

The PMR spectra of thiopyrylium, pyrylium and N-ethylpyridinium perchlorates measured in trifluoroacetic acid solution are illustrated in Fig 3. The spectrum pattern of the thipyrylium cation remains unchanged by the changes of solvents (SO_2 or DMSO), and counter anions (fluoroborate or iodide). The spectrum of the thiopyrylium cation differs substantially from those of two other cations in two respects: (1) the appearance of a pair of α-hydrogens at exceedingly low field (δ 10·20), contrary to the expectation that the pyrylium cation should possess the α-hydrogen resonance absorption in the lower field compared to that of the thio-

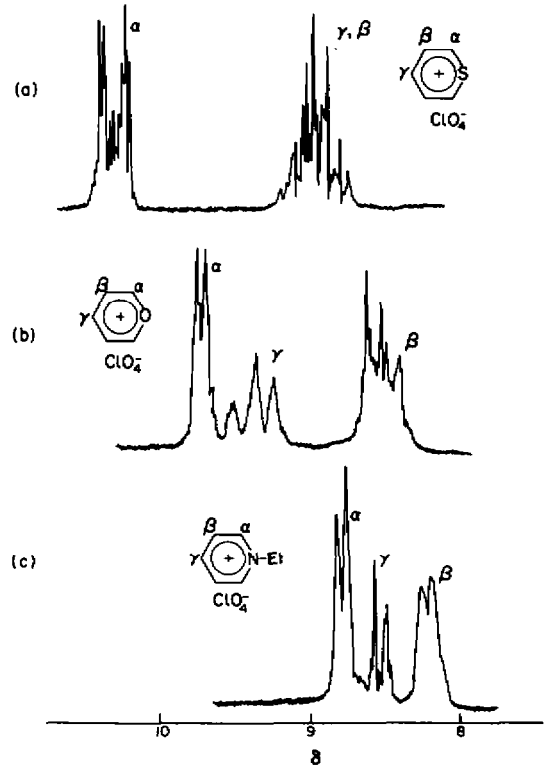
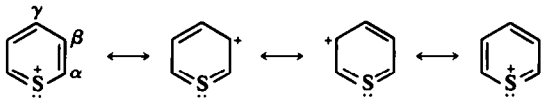
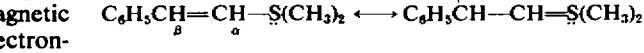


Fig 3. Proton NMR spectra of (a) thiopyrylium, (b) pyrylium and (c) N-ethylpyridinium perchlorates in trifluoroacetic acid solution at 60 MHz.

pyrylium cation, since the former has much more contribution of the carbonium ion structures than the latter; and (2) the essential superposition of the γ and β hydrogen resonances (δ 9·11). The first phenomenon is considered to arise from the magnetic anisotropic effect of the S atom and/or the electronic effects of thiopyrylium cation. However, the second, i.e. the superposition of the γ and β hydrogen resonance by the low field shift of the β hydrogens is no doubt due to the strikingly deshielding influence of the β hydrogens owing to the decreased electron densities at the β carbons, since the magnetic anisotropic effect of the S atom is expected to be negligibly small at the β hydrogens. In order to explain the decreased electron densities at the β carbons, the electron transfer from the β carbons to the S atom should occur to some extent through overlap of the α carbon 2p orbitals with the unoccupied 3d orbitals of the S atom, as shown in the following contributing structures.



The (p–d)π bonding contribution can not be involved in the resonance structures of pyrylium and pyridinium cations, and since both the cations show the proton NMR spectra expected from the (p–p)π bonding structure (Fig 3). The problem of this type of (p–d)π bonding has been recently discussed using the PMR spectroscopy in the case of dimethylstyrylsulfonium salts.[24] The low-field shifts of β-vinyl protons observed in the PMR spectra of the sulfonium salts compared with those of its corresponding ammonium salts have been attributed to the contribution of the following bonding involving sulfur 3d orbitals.



Bonding in the thiopyrylium cation. The 3d orbital involvement in the bonding scheme is expected to cause (1) the striking decrease of electron density at β-carbons, in particular due to the electron transfer from the β-carbons to the S atom, and (2) the increase of bonding between the S atom and α-carbons. These problems, which are partly supported by experimental observations, were examined by extended Hückel MO computations. Although the quantitative agreement of the extended Hückel results with experimental findings might be questioned, it is indicated that the calculated structural properties of the thiopyrylium cation distinctly varies with the contribution of the sulfur 3d orbitals to the bonding scheme.

At first we can see the dramatic effect of including S3d orbitals in the basis set at the extended Hückel charge distributions of the thiopyrylium cation. Of course, the net atomic charges (signed numbers) are parameter-dependent, but the effect of 3d orbital participation is clearly illustrated by these calculations. Fig 4 shows the relevant parts of the π and $\sigma + \pi$ atomic population analyses for the cation. The qualitative argument offered above is substantiated. In the case without 3d orbitals in the basis set, the charge densities on the C atoms have strikingly irregular values. However, in the case with 3d orbitals in the basis set, the charge irregularity is greatly reduced due to the electron transfer from the carbon fragment, particularly β-carbons,

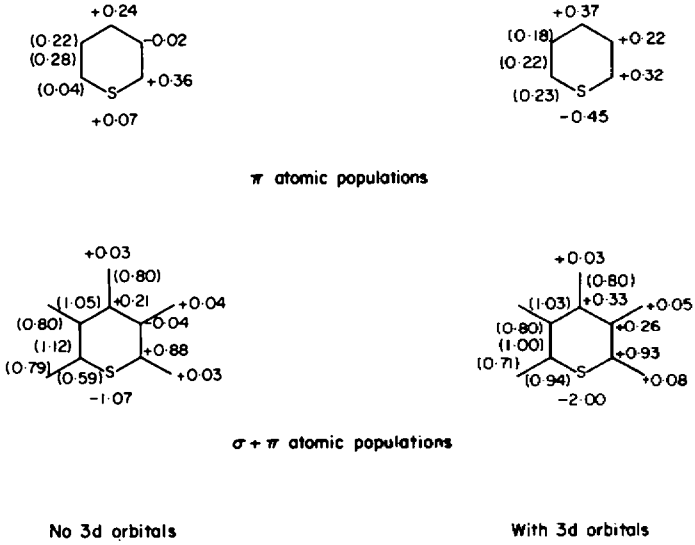


Fig 4. Mulliken population analyses of the extended Hückel numbers are not atomic charges of the nonhydrogenic atoms and bracketed numbers are overlap populations.

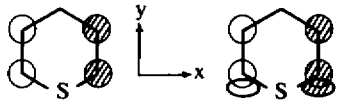
to the S atom. It is noticeable that such an electron transfer due to the 3d orbital inclusion is essentially owing to π-type interaction of C_{2pz} orbitals with unfilled S_{3dxz} and S_{3dyz} orbitals from the analyses of π and $\sigma+\pi$ atomic populations. Furthermore, we would like to point out the significant increase of the sulfur and α-carbon bond order in consequence of 3d inclusion, being responsible for the stabilization of the cation: sulfur and α-carbon overlap populations are 0·23 for π and 0·94 for $\sigma+\pi$ when 3d orbitals are included, whereas 0·04 and 0·59, respectively, without 3d orbitals.

The sulfur 3d orbitals participation may be found not only in the atomic populations illustrated above, but also even more directly in the energy and composition of the occupied molecular orbitals of the cation.

We can construct an energy diagram (Fig 5) representing the no 3d molecular orbitals of thiopyrylium cation and the 3d atomic orbitals of the S atom which are allowed by symmetry to interact with these orbitals. Inspection of Fig 5 shows the impact of 3d orbitals. It is apparent that the 3d orbitals have the most striking impact on the highest occupied MO of A_π symmetry. Whereas, the 3d orbitals have only a small stabilizing effect on the other occupied MOs, at the best by 0·23 eV. In the absence of 3d orbitals the highest occupied MO is composed of the following combinations of atomic orbitals $0{\cdot}457(C_2, 2p_Z) + 0{\cdot}457(C_3, 2p_Z) - 0{\cdot}457(C_5, 2p_z) - 0{\cdot}457(C_6, 2p_z)$.

Its one-electron energy is $-12{\cdot}65$ eV. Upon inclusion of 3d orbitals in the basis set the orbital is definitely stabilized by the $3d_{xz}$ atomic orbital of A_π symmetry, and its composition changes to $-0{\cdot}299(S_1, 3d_{xz}) + 0{\cdot}432(C_2, 2p_z) + 0{\cdot}348(C_3, 2p_z) - 0{\cdot}348(C_5, 2p_z) - 0{\cdot}432(C_6, 2p_z)$.

It has been stabilized as a result of 3d orbital mixing, now being located at $-13{\cdot}15$ eV in energy.



no 3d orbitals with 3d orbitals

Variation of 3d *orbital participation with the charge on the sulfur.* In the problem on the 3d orbital participation of the thiopyrylium cation we must now examine the changes in charge distributions which are very important for the cation investigated. As shown above, the thiopyrylium cation is considered as a resonance hybrid of the Kekulé-type (sulfonium ion) and carbonium ion structures. If the carbonium ion structures contribute predominantly

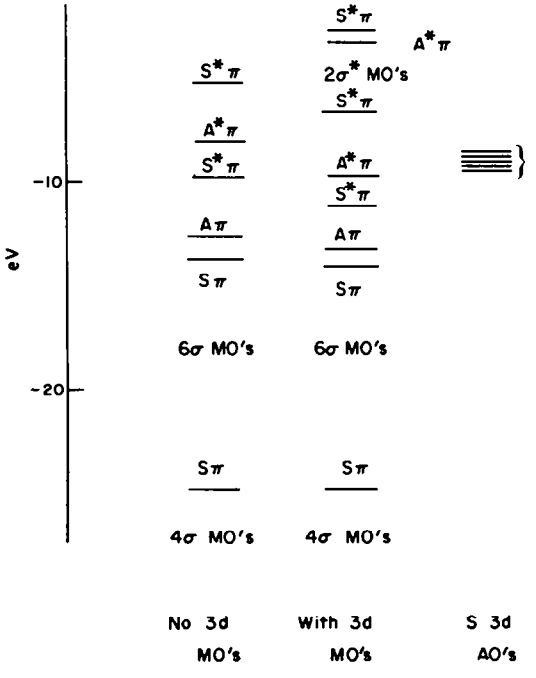


Fig 5. Orbitals for the no 3d cation (left), sulfur 3d (right), and 3d including cation. The label for A donates symmetric or antisymmetric, respectively, with respect to a plane perpendicular to the σ plane and containing the twofold axis of S_1–C_4.

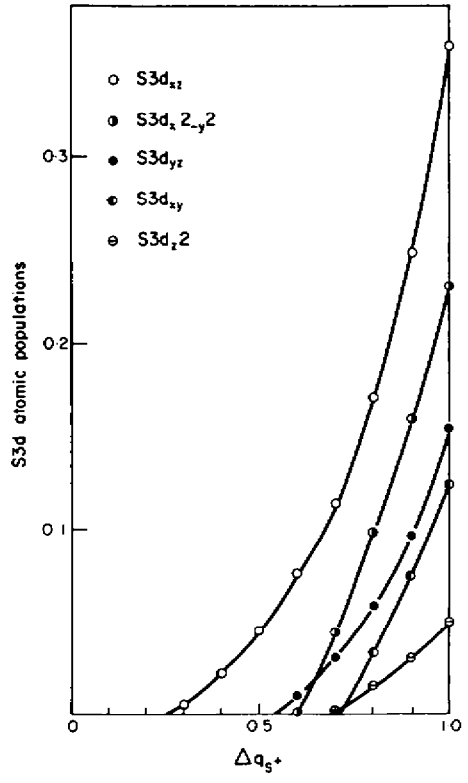


Fig 6. Change of sulfur 3d atomic population by Δq_{S^+}.

to the resonance hybrid at the ground state, the overlap of 3p sulfur orbital with adjacent 2p orbitals (type 1) is important. Whereas, in the case of the predominant contributions of sulfonium ion structures, the 3d orbitals of the S atom can overlap effectively with neighboring 2p orbitals (type 2).

$$-\overset{+}{C}-\ddot{S}- \longleftrightarrow -C=\overset{+}{\ddot{S}}- \quad (1)$$

(2p–3p)π

$$-C=C-\overset{+}{\ddot{S}}< \longleftrightarrow -\overset{+}{C}-C=\underset{\cdot\cdot}{S}< \quad (2)$$

(2p–3d)π

As expected the 3d orbital participation will be decreased sharply according as the increase of the contribution of the carbonium ion structures. The 3d orbital participation by changing the charge distributions was examined using extended Hückel MO computations. We estimated the diagonal terms (H_{ii}) for the Δq_{S+} and Δq_{C+} charged S and C atoms, respectively, as follows.

$$H(3s)_S = -20{\cdot}08 - 15{\cdot}10\Delta q_{S+}$$
$$H(3p)_S = -13{\cdot}32 - 11{\cdot}17\Delta q_{S+}$$
$$H(3d)_S = -2{\cdot}007 - 6{\cdot}766\Delta q_{S+}$$
$$H(2s)_C = -21{\cdot}01 - 12{\cdot}02\Delta q_{C+}$$
$$H(2p)_C = -11\ 27 - 12{\cdot}66\Delta q_C$$

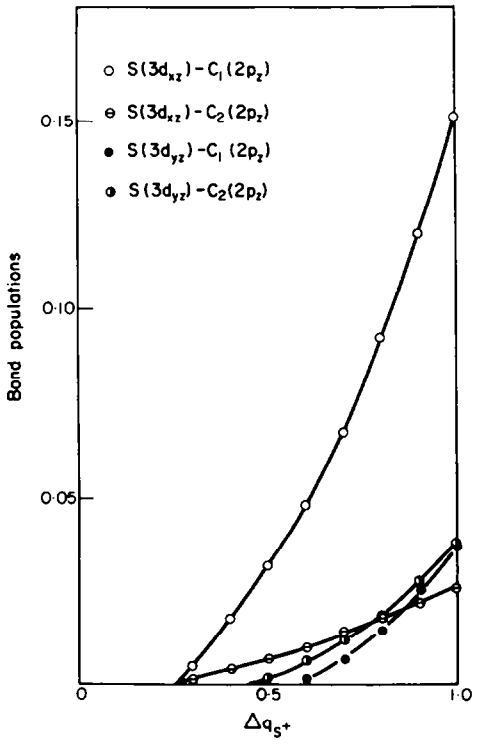


Fig 7. Change of bond populations $S(3d_{xz})$–$C_1(2P_z)$, $S(3d_{yz})$–$C_1(2p_z)$, $S(3d_{xz})$–$C_2(2p_z)$ and $S(3d_{yz})$–$C_2(2p_z)$ by Δq_{S+}.

where Δq_{S+} and Δq_{C+} represent the formal charge on a S or a C atom, respectively. The plots of sulfur 3d atomic populations, and overlap populations of sulfur $3d_{xz}$, $3d_{yz}$ orbitals and the $2p_z$ orbitals on carbon 1 and 2 *vs* the formal charge on a S atom are shown in Figs 6 and 7, respectively. These data clearly indicate that the sulfur 3d orbital participation diminishes sharply according to the decrease of the formal charge on a S atom, and for $\Delta q_{S+} = 0{\cdot}3$ such participation is negligibly small.

Conclusions. These calculations predict that the sulfur 3d orbitals participate importantly to the bonding scheme of the thiopyrylium cation, and are responsible for its thermal stability and its characteristic electronic structure. However, for predicting the degree of 3d orbital participation these calculations are inconclusive until the experimentally determined structure of the thiopyrylium cation is determined.

Acknowledgement—We are greatly indebted to Dr. Hirohiko Sugimoto (Shionogi Company Ltd.) for his assistance in making the program and for his stimulating discussion.

REFERENCES

[1a]J. Koutecky, Collection Czeckoslov. *Chem. Commun.* **24**, 1608 (1959); [b]R. Zahradnick and J. Koutecky, *Tetrahedron Letters*, 632 (1961)
[2]M. H. Plamer and R. H. Findlay, *Ibid.*, 4165 (1972)
[3]A. T. Balaban and Z. Simon, *Tetrahedron* **18**, 315 (1962)
[4]R. G. Turnbo, D. L. Sullivan and R. Pettit, *J. Am. Chem. Soc.* **86**, 5630 (1964)
[5]F. Klages and H. Trager, *Chem. Ber.* **86**, 1327 (1953)
[6]S. Oae, 3d *Orbital Resonance Involving the Sulfur Atom in Organic Sulfides*, in *Organic Sulfur Compounds* (Edited by N. Kharash) Vol. 4. Pergamon Press, Oxford (1961)
[7]I. Degani, R. Fochi and C. Vincenzi, *Gazz. Chim. Ital.* **94**, 203 (1964)
[8]N. Menschutkin, *Z. Physik. Chem.* **5**, 589 (1890)
[9a]R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.* **36**, 2179, 3489 (1962); [b]R. Hoffmann and W. N. Lipscomb, *Ibid.* **37**, 2872 (1962); [c]R. Hoffmann, *Ibid.* **39**, 1397 (1963)
[10a]J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.* **84**, 540 (1962); [b]*J. Phys. Chem.* **67**, 1501 (1963)
[11]L. C. Cusachs and J. R. Linn, *J. Chem. Phys.* **46**, 2919 (1967)
[12]M. Wolfsberg and L. Helmholtz, *Ibid.*, **20**, 837 (1952)
[13]R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *Ibid.* **17**, 1248 (1949)
[14]M. D. Newton, F. P. Boer and W. N. Lipscomb, *J. Am. Chem. Soc.* **88**, 2367 (1966)
[15a]D. P. Santry and G. A. Segal, *J. Chem. Phys.* **47**, 158 (1967); [b]D. P. Santry, *J. Am. Chem. Soc.* **90**, 3309 (1968); [c]D. P. Craig and E. A. Magnusson, *J. Chem. Soc.* 4895 (1956)
[16a]D. W. J. Cruickshank, *J. Chem. Soc.* 5486 (1961); [b]D. W. J. Curickshank, B. C. Webster and D. F. J. Mayers, *Ibid.* **40**, 733 (1964); [c]D. W. J. Cruickshank, B. C. Webster and M. A. Spinnler, *Int. J. Quant. Chem.* **1s**, 225 (1967); [d]D. P. Craig and T. Thirunamachandran,

J. Chem. Phys. **45**, 3355 (1966); [c]G. S. Chandler and T. Thirunamachandran, *Ibid.* **47**, 1192 (1967)
[17]G. Burns, *Ibid.* **41**, 1521 (1964)
[18]R. D. Brown and J. B. Peel, *Aust. J. Chem.* **21**, 2589 (1968)
[19a]D. T. Clark, *Tetrahedron* **24**, 2663 (1968); [b]R. D. Brown and J. B. Peel, *Aust. J. Chem.* **21**, 2617 (1968)
[20]D. P. Santry and G. A. Segal, *J. Chem. Phys.* **47**, 158 (1967)
[21]D. P. Craig and C. Zauli, *Ibid.* **37**, 601, 609 (1962)
[22a]F. Agolini, S. Klemenko, I. G. Csizmadia and K. Yates, *Spectrochim. Acta* **24**, 169 (1968); [b]K. Yates, S. Klemenko and I. G. Csizmadia, *Ibid.* **25**, 765, (1969); [c]G. H. Schmid and J. Bertran, *Int. J. Sulfur Chem.* A, **1**, 12 (1971)
[23a]J. Fabian, A. Mehlhorn and R. Zahradnik, *J. Phys. Chem.* **72**, 3975 (1968); [b]Z. Yoshida, H. Sugimoto and S. Yoneda, *Tetrahedron* **24**, 5873 (1972)
[24]M. C. Caserio, R. E. Pratt and R. J. Holland, *J. Am. Chem Soc.* **88**, 5747 (1966)