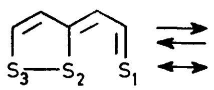
# Model Calculations on Thiocarbonyl Systems

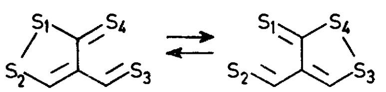
By **Gion Calzaferri** and **Rolf Gleiter**,*† Physikalisch-Chemisches Institut der Universität Basel, Basel, Switzerland

The potential surface for the valence tautomerism of 4-thioformyl-1,2-dithiole-3-thione (2) is investigated using the extended Hückel method. The different paths from one isomer to the other and individual aspects of the potential surface are discussed. It is found that in (2) the energy difference between a structure of $C_{2v}$ symmetry and $C_s$ symmetry is *ca.* 35 kcal mol$^{-1}$ due to the non-linear arrangement of the four sulphur atoms. Other systems containing thiocarbonyl groups have been investigated with regard to possible valence tautomerism.

WHILE in the thiathiophthen system (1) the evidence for a tautomerism is circumstantial and still open to debate,[1] in the related system 4-thioformyl-1,2-dithiol-3-thione (2), Brown *et al.*[2] have proven the existence of the tautomerism (2) by n.m.r. spectroscopy. These authors found two methyl singlets in the n.m.r. spectrum

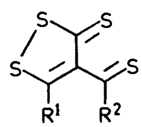



(1a) (1b) (1)




(2a) (2b) (2)

of (I). However attempts to prepare (II) and (III) gave identical products which, as shown by their n.m.r.




(I) $R^1 = R^2 = p\text{-}MeC_6H_4$
(II) $R^1 = Ph$, $R^2 = p\text{-}MeC_6H_4$
(III) $R^1 = p\text{-}MeC_6H_4$, $R^2 = Ph$

spectra, were mixtures of the two isomers. This led to the conclusion that 'isomeric thioacyl compounds ($R^1 \neq R^2$) are interconvertible but that the tautomeric equilibrium is not rapidly established (on the n.m.r. time-scale) at room temperature.' [2]

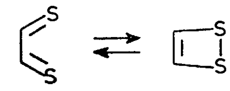
We thought it worthwhile to investigate the potential energy surface of (2) and related systems to find out if there is a fundamental difference between (1) and (2).

† *Present address*: Institut für Organische Chemie der Technischen Hochschule Darmstadt, D61 Darmstadt, W. Germany.

‡ For the molecular orbital calculations the following geometrical parameters were assumed and kept constant during the calculation: C–C = 1·4 Å, C–S = 1·7 Å, C–H = 1·1 Å, and $\widehat{C\text{–}C\text{–}H}$ = 120°. For the calculation with the extended Hückel method the Slater exponents and ionization potentials for H, O, and C were those used by Hoffmann except for a Slater exponent of 1·3 for H. The Slater exponents for sulphur were taken from Clementi and Raimondi [5] except for the sulphur 3*d*-orbitals which were estimated as 1·6. The valence state ionization potentials of sulphur were estimated as $H_{ii}(3s) = -20{\cdot}0$, $H_{ii}(3p) = -13{\cdot}3$, and $H_{ii}(3d) = -6{\cdot}0$ eV. Although the EH method has numerous documented deficiencies, it does seem to capture the essence of energetic change in angle distortions within molecules. Therefore we varied only the C–C–S angles. The C–C–C and C–C–H angles were only varied in the minima and saddle points. In all calculations reported, the results for the latter variations were omitted for the sake of clarity since no significant change was found. For the CNDO/2 method we used the parameters suggested by Pople *et al.*[6] The parameter used for sulphur was the *sp* basis set referred by Santry and Segal.[6]

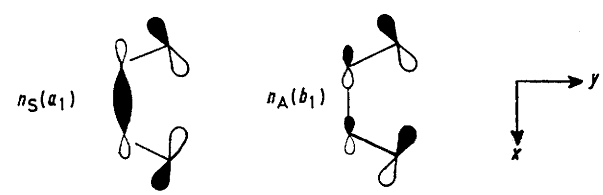
Before we discuss (2), which is rather large and has only $C_s$ symmetry we prefer to examine the essential features of reaction (2) using a simpler system as a model.

*Model Calculations on Dithioglyoxal.*—The dithioglyoxal–1,2-dithiet system (3) is the simplest one to exhibit tautomerism between a pair of thiocarbonyl groups and an S–S bond. On each sulphur centre in




(3a) (3b) (3)

(3a) we take into account one 3*p* lone pair. The resulting two lone pairs in (3a) interact with each other and with the σ-framework yielding nonequivalent semilocalized molecular orbitals.[3] We obtain a symmetric [$n_S(a_1)$] and an antisymmetric [$n_A(b_1)$] combination of the two 3*p*-orbitals on sulphur. In Figure 1 we show the correlation between the orbitals of *cis*-dithioglyoxal and dithiet for the least motion reaction. The orbital energies were taken from an extended




Hückel (EH) [4] calculation.‡ The $n_A$ combination correlates with the S–S σ*-orbital and thus crosses the $n_S(a_1)$, $\pi_3(b_2)$, and $\pi_4(a_2)$ orbitals. Thus the least motion process is a forbidden [$_\pi 2_s + _\pi 2_s$] reaction.[7] The total energy of the system as a function of the S ··· S distance is shown in Figure 2(a) according to an EH calculation [4,‡] and in Figure 2(b) according to a CNDO/2 calculation.[6,‡] Both methods predict that the

[1] E. Klingsberg, *Quart. Rev.*, 1969, **23**, 537; N. Lozac'h, *Adv. Heterocyclic Chem.*, 1971, **13**, 161.
[2] E. I. G. Brown, D. Leaver, and T. J. Rawlings, *Chem. Comm.*, 1969, 83.
[3] J. R. Swenson and R. Hoffmann, *Helv. Chim. Acta*, 1970, **53**, 2331; D. O. Cowan, R. Gleiter, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Angew. Chem.*, 1971, **83**, 405; *Angew. Chem. Internat. Edn.*, 1971, **10**, 401.
[4] R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397; R. Hoffmann and W. N. Lipscomb, *ibid.*, 1962, **36**, 2179, 3489; 1962, **37**, 2872.
[5] E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, 1963, **38**, 2686.
[6] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970 and references therein; D. P. Santry and G. A. Segal, *J. Chem. Phys.*, 1967, **47**, 158.
[7] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, 1969, **81**, 797.

level crossing occurs between 2·8 and 2·9 Å, but they differ considerably in predicting which is the more stable isomer. While the EH method favours (3a) as the more stable isomer, the CNDO/2 method predicts that (3b) is considerably more stable than (3a).

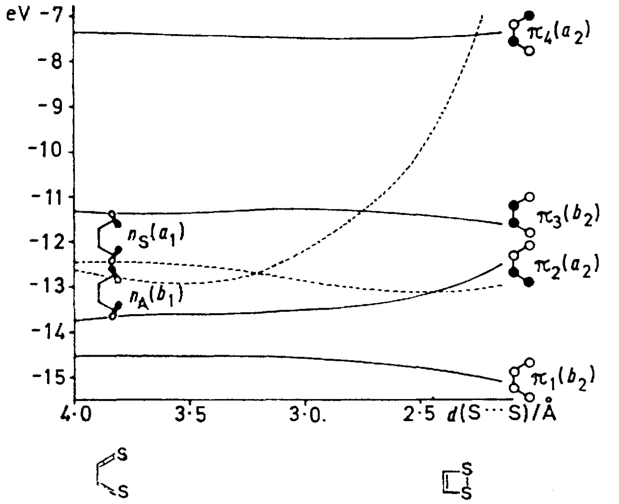



FIGURE 1 Molecular orbitals of (3) as a function of the S · · · S distance derived from an EH calculation. Four orbitals are occupied

The EH results are in good agreement with experimental results on 4,4′-bis(dimethylamino)dithiobenzil for which an equilibrium with its valence tautomer was found.[8] The discrepancy of the CNDO/2 result with experiment is sizeable, probably because this method tends to overestimate the stability of small rings.[9] In view of this discrepancy we did not pursue calculations with the CNDO/2 method any further.

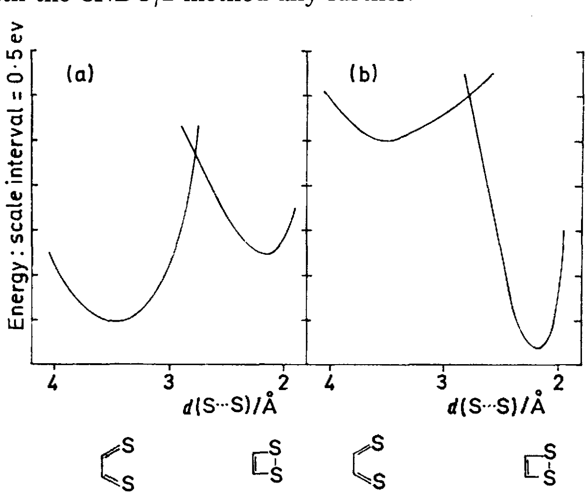
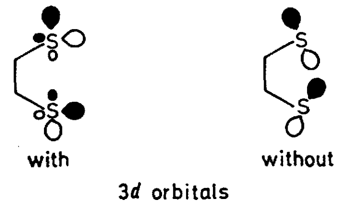



FIGURE 2 Total energy of (3) as a function of the S · · · S distance according to an EH calculation (a) and a CNDO/2 calculation (b)

The inclusion of 3d-orbitals does not qualitatively change any of these results. The sharp rise in energy of the $n_A$ combination is less pronounced by mixing in $3d_{x^2-y^2}$ but $\pi_3$ is also lowered in energy. As anticipated the level crossing between $n_A(b_1)$ and $\pi_3(b_2)$ has a




large effect on the charge distribution and the Mulliken overlap population[10] of the molecule. Decreasing the S · · · S distance from 4·0 to 2·0 Å transfers electron density from the sulphur to the carbon atoms and the C–C and S–S overlap populations are increased while the C–S overlap population is decreased. These effects, most pronounced at 2·7 Å, are illustrated in Figures 3(a) and (b). The charges and bond indices[11] obtained with the CNDO/2 method show qualitatively the same trends as shown in Figure 3.

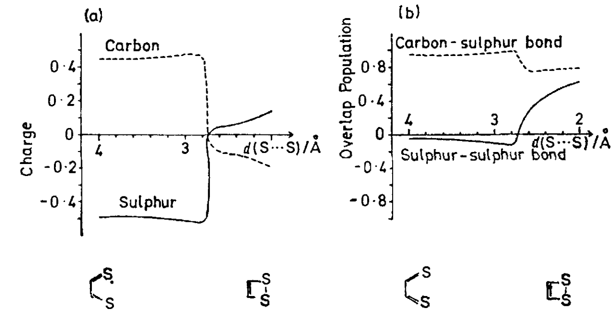



FIGURE 3 (a) Net charges on the carbon and sulphur atoms of (3) as a function of the S · · · S distance as derived from an EH calculation. (b) Overlap population between the sulphur atoms and the carbon and sulphur atoms of (3) as a function of the S · · · S distance

The cusp in Figure 2 can be avoided if the reaction proceeds *via* a transition state with $C_2$ symmetry, *i.e.* a symmetry allowed $[_\pi 2_s + _\pi 2_a]$ process[7] or by lowering $\pi_3$ (see Figure 1) below the $n_A$ combination. In the first case the $n_A$ combination correlates with the $\pi_3$ orbital and thus the cusp is smoothed. In the second case there should be a very flat minimum in the total energy function at small S · · · S distances. This minimum is due to a compensation of the rising $\pi_2$ and the descending $n_S$ and $\pi_1$ orbitals. In general there are two ways to achieve a lowering of $\pi_3$ below the $n_A$ combination either by inductive effects or by a low lying $\pi^*$ orbital of $b_2$ symmetry. These conclusions are in line with the HMO calculations carried out by Simmons *et al.*[12] on (3a and b), substituted by electron-releasing (*e.g.* $NMe_2$, Me) and attracting groups (*e.g.* $CF_3$, CN). These authors found that electron-releasing groups stabilize the dithiocarbonyl structure relative

[8] W. Küsters and P. de Mayo, *J. Amer. Chem. Soc.*, 1973, **95**, 2383; 1974, **96**, 3502.
[9] E. I. Snyder, *J. Amer. Chem. Soc.*, 1970, **92**, 7529.
[10] R. S. Mulliken, *J. Chem. Phys.*, 1955, **23**, 1833, 1841, 2338, 2343. In the first paper of this group the occurrence of negative values for the overlap population is commented on.
[11] K. B. Wiberg, *Tetrahedron*, 1968, **24**, 1083.
[12] H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *J. Amer. Chem. Soc.*, 1962, **84**, 4756 and following papers.

to the dithiet structure while electron-withdrawing substituents stabilize the cyclic structure (3b) relative

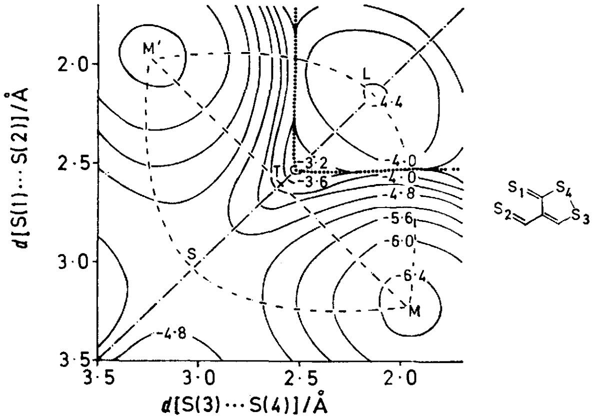



FIGURE 4 Contour diagram of the EH potential surface for (2). The contours are drawn every 0·4 eV. The dotted line indicates a ridge. The paths from minimum M to M′ *via* the saddle point S, the local minimum L, and the path for a concerted reaction *via* T are indicated

to the open form (3a). The preparation of bispolyfluoroalkylated dithiet by Krespan *et al.*[13] corroborates these conclusions.

in the model system described by equation (3), it is very likely that path (iii) will show crossing between a low-lying empty $\pi$ orbital and the antibonding lone pair combination at S(1) and S(2), making this path less favourable. It is difficult to estimate which of the other two paths has the lowest activation energy. To determine this we have explored the potential surface of equation (2) by varying the S(1) ··· S(2) and S(3) ··· S(4) distances independently. All the other distances were left constant. The potential surface for equation (2) using the EH method is shown in Figure 4. This Figure shows two broad minima M and M′ which are related by symmetry. Minimum M corresponds to structure (2b), M′ to (2a). The three paths (i)—(iii) are indicated by broken lines. The ridge due to crossing of a low lying empty $\pi$ orbital and an occupied lone pair combination is indicated by dots. Besides M and M′ three further points are set forth in Figure 4: the local minimum L in the upper right corner, the saddle point S near the lower left corner, and the transition state, T, for the concerted reaction which is in the centre of the Figure. Very close to T one finds the highest point of the surface, *ca.* 3·3 eV above M and M′.

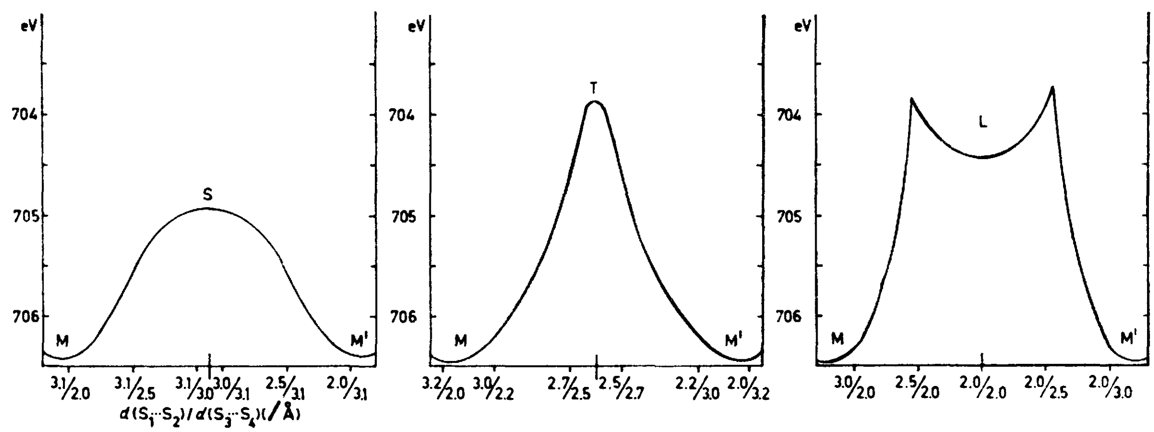
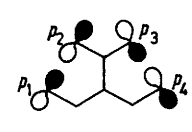



FIGURE 5 Energy profiles along the paths M–S–M′, M–T–M′, and M–L–M′ of Figure 4

*Potential Surface for* (2).—The valence tautomerism (2) is more complicated. There are at least two non-synchronous and one synchronous path for the narcissistic reaction[14] (2) providing all C–C and C–S bond lengths are not changed. These three paths are: (i) starting from (2b), the bond S(3) ··· S(4) is lengthened until both distances S(1) ··· S(2) and S(3) ··· S(4) are equal ($C_{2v}$ symmetry), then the S(1) ··· S(2) bond is shortened to isomer (2a); (ii) a concerted path is followed: while S(3) ··· S(4) is lengthened, S(1) ··· S(2) is shortened; and (iii) the bond S(1) ··· S(2) is shortened until both distances S(1) ··· S(2) and S(3) ··· S(4) are equal ($C_{2v}$ symmetry), then S(3) ··· S(4) is lengthened.

From our consideration of the valence tautomerism

In Figure 5 the energy profiles along the different paths are depicted. Both figures clearly display that path (i) has the lowest energy. The activation energy for (2) (energy difference between M and S) was calculated as 1·5 eV. This value compares well with the experimental findings of Brown *et al.*[2] To understand the hypersurface for (2) we consider the four possible combinations of the four $3p$ orbitals of the sulphur atoms, S(1)—S(4). If we define $p_1$, $p_2$, $p_3$, and $p_4$ as shown, we obtain in a ZDO approximation:




$C_{2v}$

$$n_S = \tfrac{1}{2}(p_1 - p_2 + p_3 - p_4) \quad a_1$$

$$n_S' = \tfrac{1}{2}(p_1 + p_2 - p_3 - p_4) \quad a_1$$

$$n_A = \tfrac{1}{2}(p_1 - p_2 - p_3 + p_4) \quad b_1$$

$$n_A' = \tfrac{1}{2}(p_1 + p_2 + p_3 + p_4) \quad b_1$$

[13] C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Amer. Chem. Soc.*, 1960, **82**, 1515; C. G. Krespan, *ibid.*, 1961, **83**, 3434.
[14] L. Salem, *Accounts Chem. Res.*, 1971, **4**, 322.

We start our discussion of the potential surface (Figure 4) representing equation (2) with a transition state of $C_{2v}$ symmetry and with distances S(1) $\cdots$ S(2) = S(3) $\cdots$ S(4) = 3·0 Å, the saddle point S of the potential surface. At this point the EH calculation reveals the following order $n_S$, $n_A$, $n'_S$, $n'_A$ (see Figure 6, left). This ordering is expected if the interaction between the lone pairs on the sulphur atoms is mainly through space and not through bonds.[15]

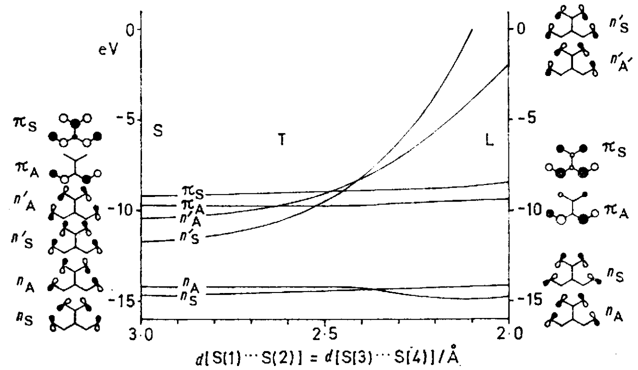



FIGURE 6 Molecular orbitals of (2) ($C_{2v}$) as a function of the S $\cdots$ S distance along the indicated diagonal of Figure 4. The energy values are derived from an EH calculation. Three molecular orbitals are occupied

If the two S $\cdots$ S bonds are shortened in such a way that $C_{2v}$ symmetry is preserved, the two lone pair combinations which are bonding (antibonding) within S(1) $\cdots$ S(2) and S(3) $\cdots$ S(4) will decrease (increase) in energy. The anticipated crossing between the highest occupied ($n'_S$) and the lowest unoccupied $\pi$ orbital ($\pi_A$) (see Figure 6) occurs at an S $\cdots$ S distance of *ca.* 2·5 Å. At distances <2·5 Å we are dealing with a 12 $\pi$-system with two S $\cdots$ S $\sigma$-bonds (see Figure 6).

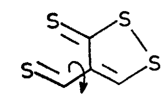
Another area of the potential surface of Figure 4 merits our attention: the local minimum L at S $\cdots$ S = 2·1—2·2 Å. This minimum can be explained by the lowering of $n_A$ during the shortening of the S $\cdots$ S distances (see Figure 6).

The two minima M and M′ which are related by symmetry (see Figure 4) can be reached either from L by lengthening one sulphur bond [path (iii)] or from the saddle point S by shortening one [path (i)]. Symmetry is lost by shortening only one S $\cdots$ S distance, say S(3) $\cdots$ S(4) but it is still possible to correlate the orbitals: the former $n_S$ orbital will emerge in a localized picture as the S(3)–S(4) $\sigma$-bond, the former $n_A$ orbital as the bonding combination $(1/2^{\frac{1}{2}})$ $(p_1 - p_2)$ the former $n_A'$ orbital as the $S(3) \cdots S(4)$ $\sigma^*$-bond and finally the $n_S'$ orbital as the antibonding combination $(1/2^{\frac{1}{2}})$ $(p_1 + p_2)$. This correlation is shown in Figure 13 and discussed in the final section.

Some points on the potential surface were calculated with the inclusion of the 3*d* orbitals on sulphur.[5] The results obtained are similar to those without 3*d* orbitals in so far as the qualitative features of the potential surface in Figure 4 are not changed.

As for the valence tautomerism (3) the overlap population and the charge density change dramatically in going from the 10$\pi$-system (M) to the 12$\pi$-system (L). The overlap population between S(1) $\cdots$ S(2) increases from −0·03 to 0·67 and the net charges at S(1) and S(2) increase from −0·87 and −0·74 to 0·22 and 0·09 respectively (compare Figures 3 and 4).

*Point* T.—The reaction along path (i) can be considered as a thermally allowed $[_{\sigma}2_a + {}_{\pi}6_s]$ or a $[_{\sigma}2_s + {}_{\pi}4_s + {}_{\pi}2_a]$ process.[7] From this point of view it follows that if we rotate *e.g.* the 4-thioformyl group out of the molecular plane, the energy of activation should be lowered compared with a planar transition state. This




is indeed the case but the gain is only 0·3 eV for a dihedral angle of 20°. For larger angles the total energy of T increases again.

*Saddle Point* S.—For the saddle point S the overlap population between the centres, S(1) $\cdots$ S(2) and S(3) $\cdots$ S(4) is 0·03 indicating a very weak S $\cdots$ S bond. This suggests investigating the possibility of a non-planar structure for S. Bending the $CS_2$ portion of (2) out of the molecular plane increases the total energy.

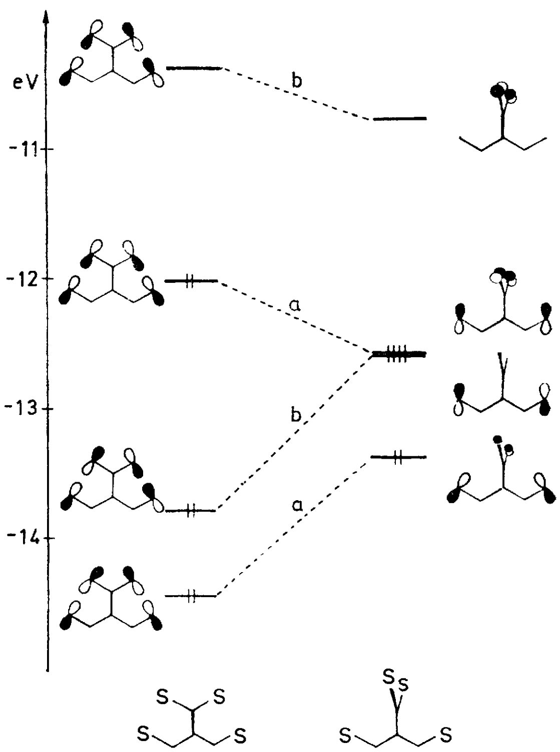


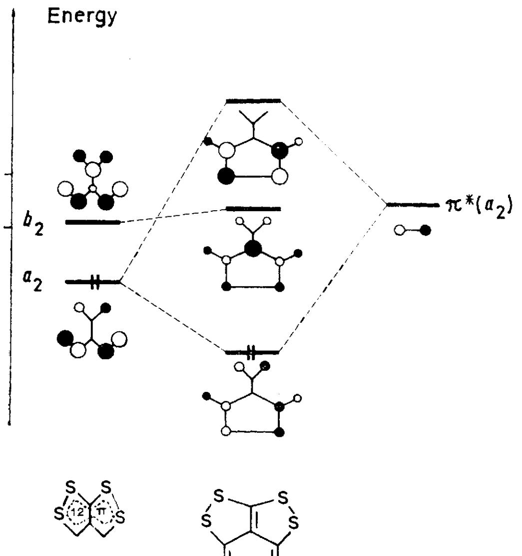

FIGURE 7 Correlation diagram between (2) in a planar geometry which corresponds to S and between (2) in a geometry where the $CS_2$ system is perpendicular to the rest of the molecule

The energy difference for S with a planar and perpendicular structure is, according to an EH calculation, 0·4 eV. In Figure 7 we have correlated the $n$-orbitals

[15] R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, 1968, **90**, 1499; R. Hoffmann, *Accounts Chem. Res.*, 1971, **4**, 1.

for both geometries.* From this diagram it is evident that in a one electron treatment a net destabilization is obtained by twisting the $CS_2$ group out of the molecular plane. Since we are dealing here with an open shell problem our results have only qualitative character and more sophisticated calculations are necessary.

*Local Minimum* L.—In Figure 8 we have indicated a possible mean of how to stabilize the local minimum L (see Figure 4). By interaction with a low lying empty orbital of $b_2$ symmetry, *e.g.* $\pi^*$ of ethylene, the HOMO is stabilized considerably. In Figure 9 the potential energy curves for the resulting system (4) are shown




L

FIGURE 8 Interaction diagram between HOMO and LUMO of L and LUMO of ethylene

along the two paths M · · · S · · · M' and M · · · L · · · M' (see Figure 4) using the EH method.[4] A structure with $C_{2v}$ symmetry is the most stable. For (5) on the other hand valence tautomerism as indicated in equation (5) is predicted.

*Potential Surface of* $C_2S_4$.—Another interesting system from the point of view of valence tautomerism is $C_2S_4$ for which some possible valence structures are shown in equation (6). This system is valence isoelectronic to dioxetandione[16] and 1,2-dimethylenecyclobutane

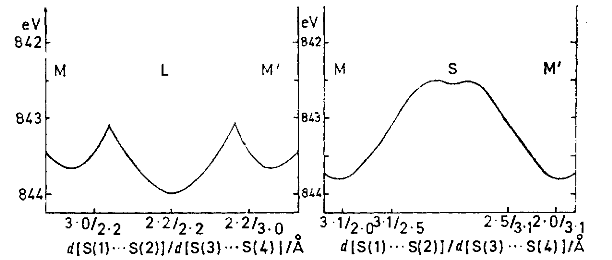
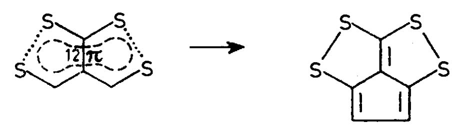


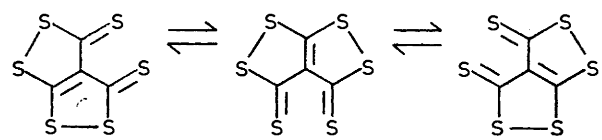

FIGURE 9 Energy profiles between M and L of compound (4) (left) and M and S of 4 (right). M, S, and L define here the same S(1) · · · S(2) and S(3) · · · S(4) distances as for system (2)

(7). The latter compound has been extensively explored theoretically[17] and experimentally.[18] It was




(4)

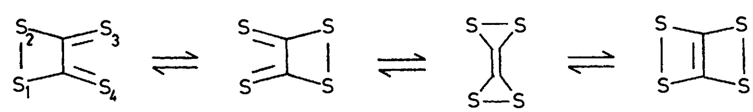
(4)



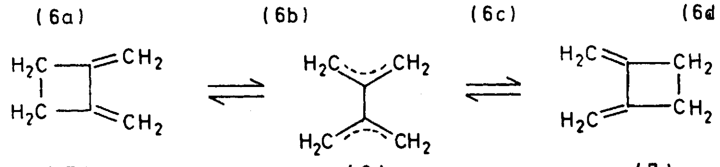
(5a) (5b) (5c) (5)

found that (7) rearranges *via* a freely rotating 2,2'-bisallyl biradical (8) which equilibrates all four methylene groups.

We have investigated the potential surface of (6) with the same constraints applied as for that of (2). The result is shown in Figure 10. The potential surface



(6a) (6b) (6c) (6d) (6)



(7) (8) (7) (7)

for (6) is similar to that of (2) in that it shows also two broad minima M and M' which correspond to the structures (6b and a) in (6). A broad pass with a saddle point S connects these two minima. In contrast to Figure 4, in Figure 10 there are two local minima, L and L' at the upper right and lower left corner. The local minimum L corresponds to structure (6c) and L'

* The change in energy for the $\pi$-orbitals is minor.

[16] H. Güsten and F. Ullmann, *Chem. Comm.*, 1970, 29.

[17] B. G. Odell, R. Hoffmann, and A. Imamura, *J. Chem. Soc.* (*B*), 1970, 1675 and references therein.

[18] J. J. Gajewski and C. N. Shih, *J. Amer. Chem. Soc.*, 1972, **94**, 1675.

to (6d). The two ridges which separate the valleys around L and L′ from M and M′ are indicated by dots. According to Figure 10 the path of minimum energy

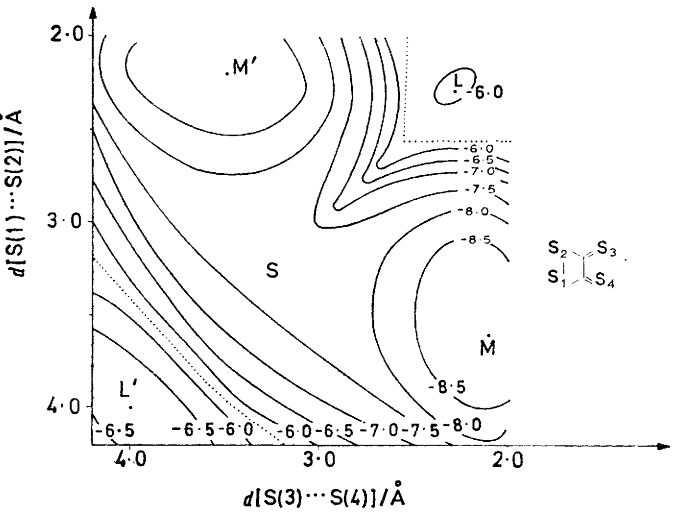



FIGURE 10 Contour diagram of the EH potential surface for (6). The contours are drawn every 0·5 eV. The dotted lines indicate a ridge. The minima M and M′ as well as the saddle point S and the two local minima L and L′ are indicated

between M and M′ is the one *via* the saddle point S. The calculated energy difference between M and S amounts to 1·4 eV.

The potential energy as a function of the S(1) · · · S(2) = S(3) · · · S(4) distance is shown in Figure 11. The cusps in Figure 11 at 2·6 and 3·8 Å correspond to the ridges in the hypersurface shown in Figure 10. Analogous to our discussion of systems (2) and (3), the two cusps in Figure 11 are due to the crossing of

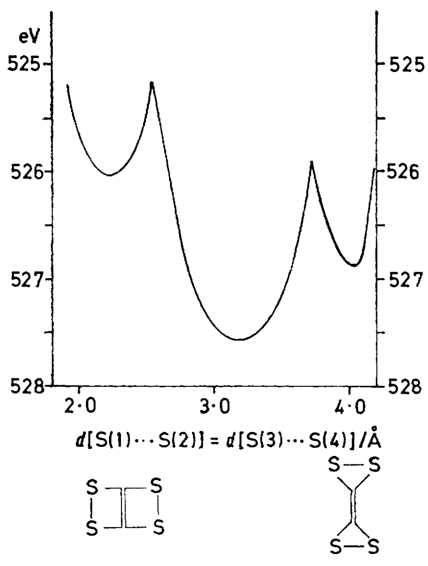



FIGURE 11 Potential energy for (6) along the diagonal through L′, S, and L ($D_{2v}$ symmetry is preserved)

an antibonding occupied lone pair combination with an unoccupied $\pi$ orbital. This crossing gives rise to a similar dramatic change in the overlap population and the charge density as discussed for (2) and (3) (*cf.* Figure 3).

The fact that (6) is valence isoelectronic with (7) suggests that a species analogous to (8) should be sought. Indeed the overlap population between S(1) · · · S(2) and S(3) · · · S(4) in the saddle point S is 0·03 and therefore a twist of the $CS_2$ group should not require too much energy.

The result of an EH calculation for (6) is that a structure with one $CS_2$ group perpendicular to the other is favoured. The energy difference between a planar structure for S and the perpendicular one just described is 0·3 eV.

In Figure 12 we have correlated the four possible combinations of the four $3p$ orbitals on the sulphur

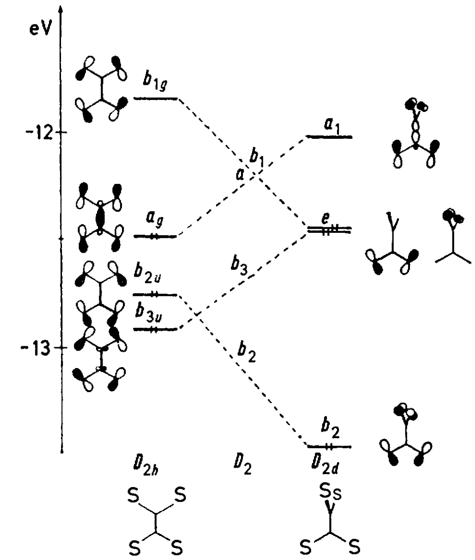



FIGURE 12 Correlation diagram between the lone pair combination on the sulphur centres of (6) in a planar geometry which corresponds to S ($D_{2h}$) and in a geometry where one $CS_2$ group is perpendicular to the other ($D_{2d}$)

atoms in $D_{2h}$ and $D_{2d}$ geometries for S(1) · · · S(2) = S(3) · · · S(4) = 3·1 Å. In contrast to a planar (2) (see Figures 6 and 7) where a through bond interaction [15] between C–C $\sigma$-orbitals and the lone pair combinations is not very important, in (6) we cannot neglect this effect. The lone pair combination of the four sulphur $3p$-orbitals which corresponds to the irreducible representation $A_g$ interacts strongly with the central C–C $\sigma$-bond. This interaction places the $a_g$ orbital on top of $b_{2u}$ and $b_{3u}$. Neglecting the through bond interaction we would have anticipated $a_g$ below $b_{2u}$ and $b_{3u}$. Although the reaction ($D_{2d} \longrightarrow D_{2h}$) is symmetry forbidden,[7] the activation energy is low, as can be seen from Figure 12. As in the case of the saddle point for reaction (2) we are dealing here with an open shell problem and for a final answer concerning the stability of the perpendicular biradical we have to wait for better calculations.

*Concluding Remarks.*—We now come back to the question we started with: Why is there a measureable activation energy for (2) and not for (1)? Semiempirical[19] and *ab initio*[20] calculations have been carried out on (1). All methods agree in so far as the energy required to distort the symmetric ($C_{2v}$) to the unsymmetric ($C_s$) system must be small. While the EH method favours a $C_s$ symmetry for (1), a minimization of the energy as a function of the geometry of (1) using the CNDO/2 method[22d] yields a structure with $C_{2v}$ symmetry. With the EH method it was found that the activation energy for valence tautomerism (1) depends considerably on the inclusion of $3d$-orbitals on sulphur. The values calculated are 1·1 without and 0·5 eV with $3d$-orbitals on the sulphur atoms. In the case of (2), however, the inclusion of $3d$-orbitals on sulphur does not decrease the value for the activation energy.

In Figure 13 we have correlated the most important $\sigma$-MOs for (1) and (2) in $C_s$ and $C_{2v}$ geometries. For (1) the slope of the correlation lines connecting the occupied orbitals is small (HOMO) or negligible. For (2), however, there is a steep ascent by the correlation line connecting the lowest occupied orbital shown in Figure 13.

This behaviour is reflected in the activation energy for the reaction $C_s \longrightarrow C_{2v}$ for (1) and (2). In case of $C_{2v}$ symmetry for (1) we can describe the bonding between the three sulphur atoms as an electron rich three-centre bond.[19a] The linear arrangement of the three

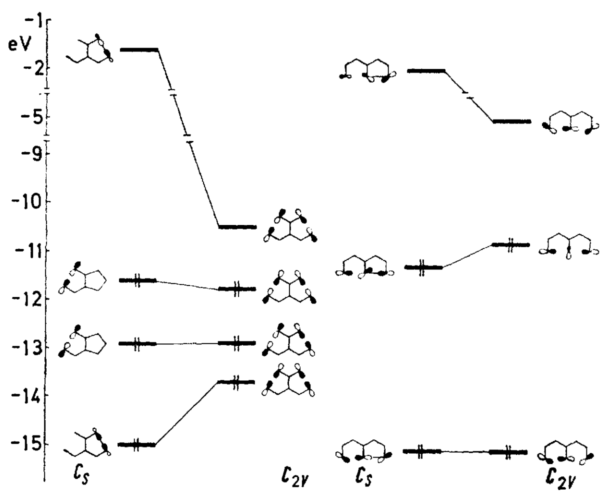
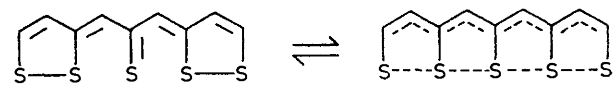
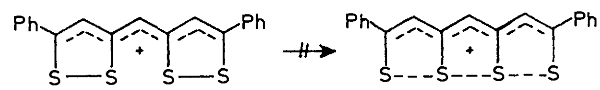



FIGURE 13 Correlation diagram between the lone pair combinations on the sulphur centres of (1) and (2) with $C_{2v}$ and $C_s$ symmetry

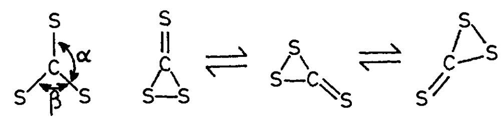
centres in (1) favours this kind of bonding and therefore the energy difference between an S(1)–S(2) $\sigma$-bond and a $3p$-lone pair on S(3) on one side and an electron rich three-centre bond between S(1), S(2), and S(3) on the other is small. In other words, the breaking of a S–S single bond (50·9 kcal mol[21]) is nearly compensated for by the electron rich three-centre bond.




(9a) (9b)




(10a) (10b)




(8)

(11a) (11b) (11c)

In case of (2), however, the electron rich four-centre bond present in S (see Figure 4) is not very favourable due to the nonlinear arrangement of the four sulphur atoms. In contrast to (1), in (2) the transition energy in going from $C_s$ to $C_{2v}$ (or M to S in Figure 5) is *ca.* 35 kcal mol$^{-1}$ according to the EH method.

To generalize this we can say that the generation of an electron rich multicentre bond, in a linear arrangement of sulphur centres, compensates approximately for the breaking of one S–S $\sigma$-bond.

This line of thinking allows us to understand, without carrying out a calculation, why in (9)[22] a structure with equal bond length (9b) between the sulphur atoms is not present.[22,23] Here the electron rich five-centre bond has to compensate the breaking of two S–S $\sigma$-bonds. As a corollary from this we expect that in $CS_3$ (11) a structure with $C_{2v}$-symmetry should be present since the formation of an electron rich three-centre bond is very unfavourable due to the nonlinear arrangement of the sulphur atoms.

Assuming that (11) is a stable and planar species and that all C–S distances remain constant in the equilibrium described by equation (8) we can specify the structure of (11) by means of the two angles $\alpha$ and $\beta$. Using the EH method[4] and varying only $\alpha$ and $\beta$ we obtain on the potential surface three minima ($\alpha = 140°$, $\beta = 80°$; $\alpha = 140°$, $\beta = 140°$; and $\alpha = 80°$, $\beta = 140°$) related by symmetry and corresponding to (11a—c).

As anticipated,[24] there exists no saddle point of $D_{3h}$ symmetry but there are three saddle points close to $D_{3h}$ symmetry * ($\alpha = 130°$, $\beta = 115°$; $\alpha = 115°$, $\beta = 130°$; and $\alpha = 115°$, $\beta = 115°$). The activation energy for the valence tautomerism described by equation (8)

* The energy difference between the structure of $D_{3h}$ symmetry and a saddle point is predicted to be 0·03 eV.

[19] (*a*) R. Gleiter and R. Hoffmann, *Tetrahedron*, 1968, **24**, 5899; (*b*) R. Gleiter, D. Werthemann, and H. Behringer, *J. Amer. Chem. Soc.*, 1972, **94**, 651; (*c*) D. T. Clark and D. Kilacast, *Tetrahedron*, 1971, **27**, 4367; (*d*) L. K. Hansen, A. Hordvik, and L. J. Saethre, *J.C.S. Chem. Comm.*, 1972, 222; (*e*) P. Bischof, unpublished results.

[20] D. T. Clark, *Internat. J. Sulfur Chem. C*, 1972, **7**, 11; M. H. Palmer, R. H. Findlay, and A. J. Gaskell, *J.C.S. Perkin II*, 1974, 420.

[21] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, 1960.

[22] E. Klingsberg, *Chem. and Ind.*, 1968, 1813; M. Stavaux and N. Lozac'h, *Bull. Soc. chim. France*, 1969, 4184.

[23] J. Sletten, *Acta Chem. Scand.*, 1970, **24**, 1464; R. Kristensen and J. Sletten, *ibid.*, 1971, **25**, 2366.

[24] J. N. Murrel and K. J. Laidler, *Trans. Faraday Soc.*, 1968, **64**, 371.

is predicted to be 1·4 eV. In Figure 14 we have correlated the highest occupied and lowest unoccupied MOs for (11) with $C_{2v}$ symmetry at the left with those for $D_{3h}$ symmetry at the right. The $C_{2v}$ species correspond to the minima (11a), (11b), and (11c) respectively. The most striking feature considering the four occupied orbitals only is the large rise of the $a_1$ orbital. This is, analogous to (2) (see Figure 13, left) due to the fact that the breaking of the S–S σ-bond affords considerable energy and there is no way to compensate for this. This correlation diagram nicely corroborates the point

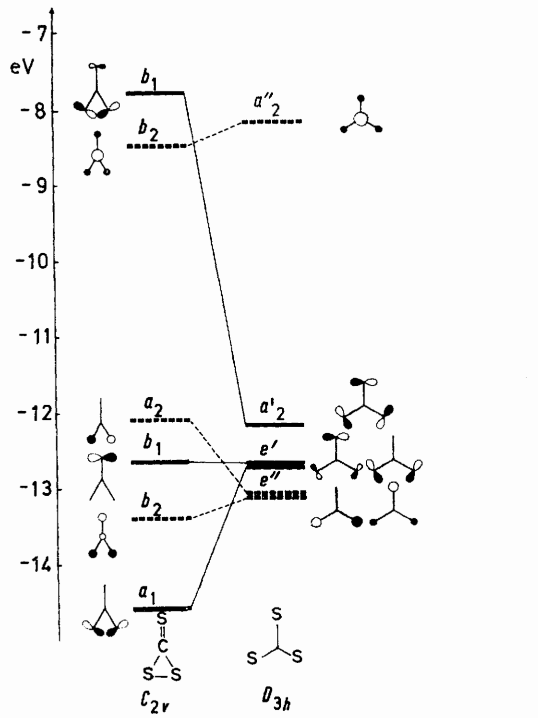
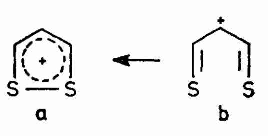



FIGURE 14 Correlation diagram between the lone pair combinations on the sulphur centres and the π-orbitals of (11) with $C_{2v}$- and $D_{3h}$-symmetry. Four orbitals are occupied

that a linear arrangement of atoms is necessary for an electron rich three-centre bond.[19a]

In the cases dealt with so far the $b_1$ ($n_A$) combination of the lone pairs on sulphur crossed an empty π orbital as the S · · · S distance is diminished (see Figures 1 and 6). Due to this crossing there are at least two minima on the potential surface, one belonging to a $4n\pi$, another one to a $(4n + 2)\pi$ system. In the example shown, only one minimum is found by varying the S · · · S distance. As can be seen from the correlation diagram in Figure 15, the $b_1$ combination never crosses the




HOMO if we precede from small (2Å) to large (3Å) S · · · S distances. The same is true for the cation (10) [25] where two short and one long sulphur bonds are observed.[26] A way to stabilize isomer b in such a case is to raise the HOMO. A filled orbital of $B_2$ symmetry

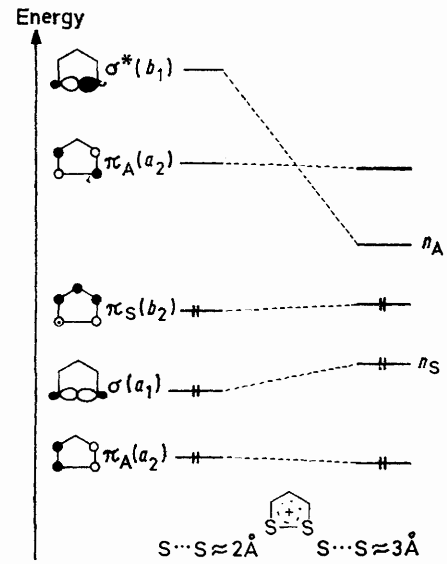



FIGURE 15 Qualitative correlation diagram of the lone pair combinations on the sulphur centres and the π-orbitals of dithiolium cation for an S · · · S distance of *ca.* 2 and *ca.* 3 Å

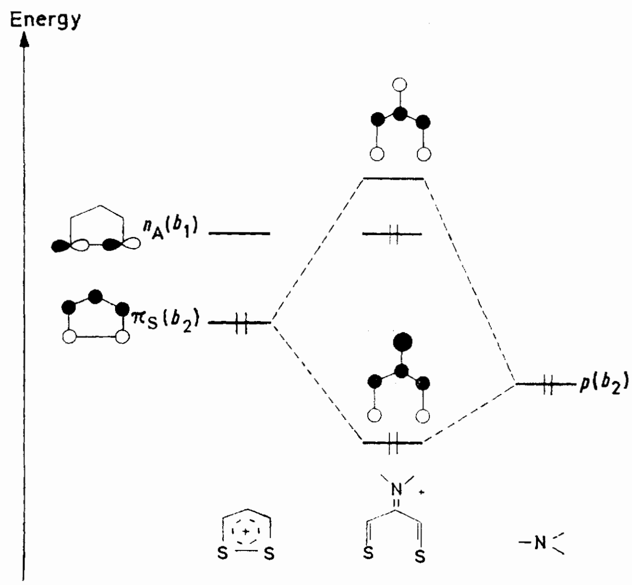



FIGURE 16 Qualitative interaction diagram between the HOMO of the dithiolium cation and a 2$p$ orbital on nitrogen

(*e.g.* the $p$-orbital of an $NH_2$ group) is a possible way to achieve this as it is shown in the interaction diagram of Figure 16.

We are most grateful to Ciba-Geigy AG (Basel) for financial support. This work is part of a project of the Schweizerischer Nationalfonds.

[4/1318 *Received*, 1st *July*, 1974]

[25] E. Klingsberg, *J. Heterocyclic Chem.*, 1966, **3**, 243.
[26] A. Hordvik, *Acta Chem. Scand.*, 1965, **19**, 1253.