(Department of Chemistry, Queen's University, Kingston, Ontario, Canada)

LUIS M. TEL

(Departamento de Quimica–Fisica, Facultad de Ciencias, Universidad de Valladolid, Spain)

and I. G. CSIZMADIA

(Department of Chemistry, University of Toronto, Toronto, Ontario, Canada)

Summary Sulphur 3*d*-orbitals are not necessary to explain the structure of dimethyl sulphide dicarbanion.

NON-EMPIRICAL molecular orbital calculations on an α-sulphinyl (I)[1,2] and an α-sulphonyl carbanion (II)[3] have revealed that in each case a pyramidal structure at carbon with the electron pair bisecting the substituents (oxygen, electron pair) on the sulphur atom represents an energy minimum. Because the results of these calculations are in satisfactory agreement with available experimental data,[4–7] the finding that[3] "the asymmetry of α-sulphinyl and α-sulphonyl carbanions need not be related to a possible existence of 3*d*-orbital conjugation" cannot be dismissed.

Extension of this work to the tautomer of thiomethoxide ion (III, HMS⁻) has produced an analogous result which we report now in view of the recent discussion by Bank and Coffen.[8] They observed ready formation of the dicarbanion (IVb) from dimethyltetrathia-adamantane (IVa), and attributed this to stabilization of 1,3-pyramidal electron pairs by a *d*-orbital of an intervening sulphur atom (their Figures 1 and 2). However, such pictorial explanations, while aesthetically pleasing, are not obligatory. The bridgehead protons of (IVa) bisect the electron pair–sulphur–electron pair angles of *two* sulphur atoms. In the case of one sulphinyl and one sulphonyl grouping this is a favourable geometry for proton abstraction; and the difference in acidity between a proton flanked by one and by two sulphonyl groups is at least nine powers of ten.[9,10]

A three-dimensional energy surface was computed for HMS$^-$ for rotation about the C–S bond (θ) and inversion of the HCH angle (ϕ) (the bond lengths and the CSH angle were those of methanethiol,[11] and the calculations were performed by the SCF–MO method using a minimal GTF basis set, as described previously[2]). Figure 1 shows the cross-section of this surface for rotation about the C–S bond (θ) through the energy minimum ($\phi = 115°$). As stated above, the conformation of HMS$^-$ which maximizes gauche interactions between adjacent electron pairs represents the energy minimum. As in the earlier work,[1–3] with this basis set there is no effective contribution to the structure from the d-orbitals of sulphur.

$^{-}{:}CH_2SHO$

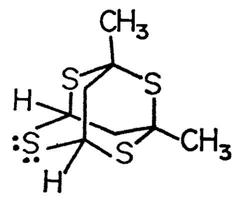
(I)

$^{-}{:}CH_2SHO_2$

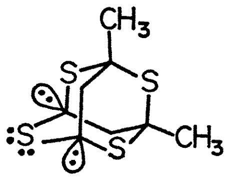
(II)

$^{-}{:}CH_2SH$

(III)

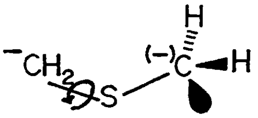


(IVa)



(IVb)

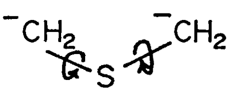
Case (i)



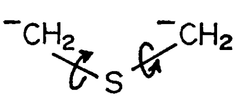
$^{-}CH_2SCH_2^{-}$

(V)

Case (ii)



Case (iii)



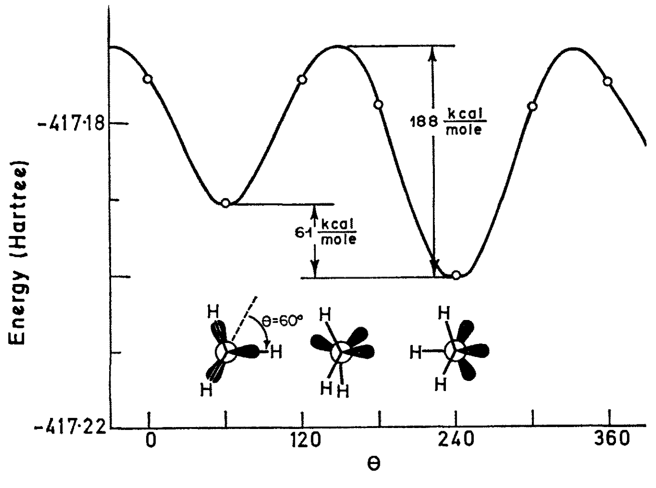


FIGURE 1. *A cross-section of the energy surface of* HMS$^-$ *for rotation about the* C–S *bond* (θ) *through the energy minimum* ($\phi = 115°$).

It can be argued that HMS$^-$ is not a satisfactory model for the situation envisaged by Bank and Coffen[8] (their Figure 2), in which a single 3d-orbital stabilizes two adjacent pyramidal carbanionic centres. Calculations were, therefore, performed on dimethyl sulphide dicarbanion (V, DMS^{2-}). The geometrical parameters were:[2,12] HCH, 115°; CSC, 105°; C–H, 1·09 Å; C–S, 1·82 Å. Three types of rotational behaviour were considered; *Case* (*i*): one C–S bond is fixed with the electron pair bisecting the two electron pairs of sulphur, and the second C–S bond is allowed to rotate; *Case* (*ii*): both C–S bonds rotate, in a disrotatory manner; *Case* (*iii*): both C–S bonds rotate, in a conrotatory manner. The results are shown in Figure 2. The relative stabilities of the computed points are A > B > C > D > E > F > G > H. The energy differences between each pair are, respectively 5·7, 5·3, 3·8, 18·2, 0·5, 3·0, and 0·3 kcal./mole. Thus, the three stable conformations (A, B, C) in which the two carbanions are placed in the plane of the bisector of the electron pair : sulphur : electron pair angle are 3·8—14·8 kcal./mole more stable than a conformation (D) in which one carbanion is in the plane of the bisector and the other is not; and this conformation is at least 18 kcal./mole more stable than any conformation (E, F, G, H) in which neither carbanion is in the plane of the bisector.

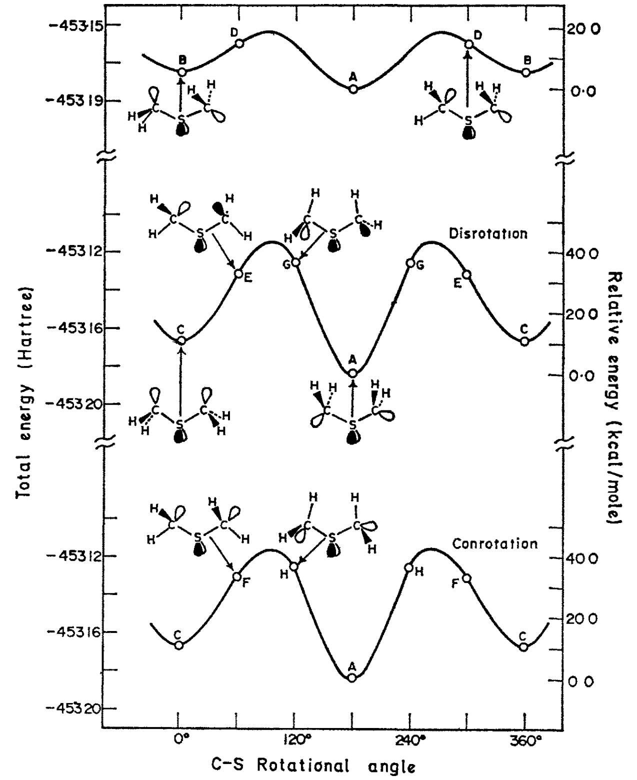


FIGURE 2. *Upper curve*: *rotation about one* C–S *bond with the second carbanion fixed on the acute bisector of the electron pair* : *sulphur* : *electron pair angle. Middle curve*: *disrotation. Lower curve*: *conrotation.*

Since, as in the other examples discussed previously (refs. 1—3 and HMS$^-$ above), the *d*-orbitals of sulphur are not necessary to explain the structure of DMS^{2-}, it is evident that electron pair–electron pair interactions play an important if not dominant role in deciding the stereochemistry of this system. Chemical intuition would then suggest a structure for DMS^{2-} in which the four electron pairs are as far apart as possible, but this is not the case. The most stable structure, A, contains *the maximum number of gauche interactions between adjacent electron pairs*.

These results indicate, therefore, that the observation of Bank and Coffen[8] can be interpreted without resort to a postulate of *d*-orbital conjugation. It may be noted further that the demonstration of the importance of electron pair–electron pair or electron pair–polar bond interactions in deciding the structures of carbanions generated next to sulphur, sulphoxide, and sulphone extends to the Second Row a stereochemical phenomenon which is now well established for atoms of the First Row.[13]

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