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CALCULATION OF CARBON-SULPHUR BOND LENGTHS

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It is possible to calculate bond lengths from the known bond orders. But, for that it is necessary to establish a relationship between bond length and bond order. Such a relationship has been established for the case of C-C bonds (1-3), and works quite well (4). There were several attempts in the past (5,6) to establish the bond length-bond order relationship for C-S bonds. Previous research workers have used HMO bond orders, and they have also assumed that the length of a double C-S bond is 1.61 Å. It appears that this value is a little too long for a double C-S bond (7).

In this communication we present a new bond length-bond order curve, which differs from previous ones because we have used SCF bond orders, and we have taken more realistic value for the length of a double C-S bond. For single and double C-S bonds average values of 1.82 Å (7) and 1.56 Å (7) respectively, are used. Our curve for the dependence of C-S bond length on double bond character is given in the Fig. The following linear equation could approximate this curve :

$$L(ij) = 1.82 - 0.26\, p(ij) \qquad (I)$$

where L(ij) is a bond length in Å, and p(ij) is calculated bond order.

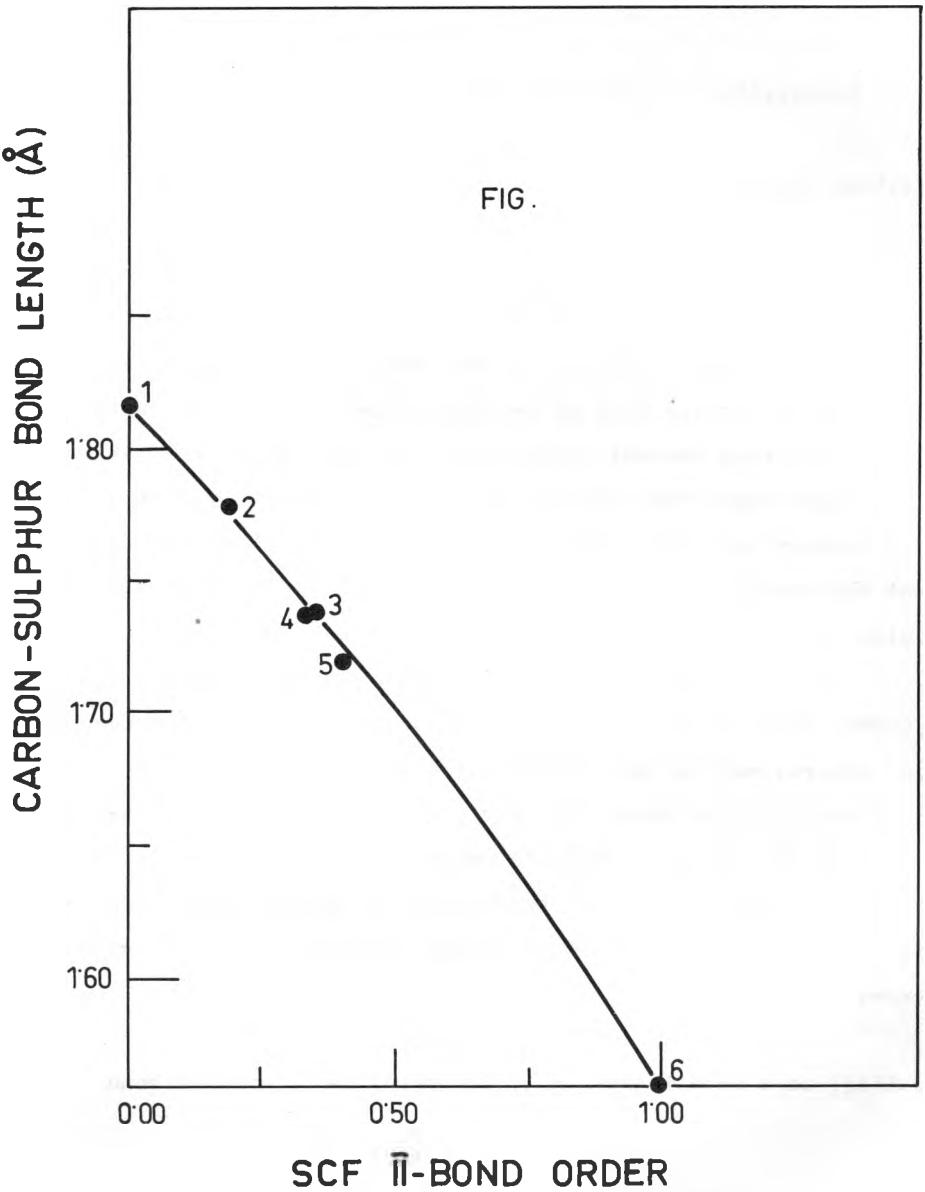
FIG.
CARBON-SULPHUR BOND LENGTH (Å)
1·80
1·70
1·60
1
2
3
4
5
6
0·00
0·50
1·00
SCF π-BOND ORDER

SCF π-bond orders and experimental and calculated values for C-S bond lengths are given in the Table.

TABLE

Comparison of Calculated and Observed Bond Lengths for $C(sp^2)$-S(II) Bonds

No. of point in the Fig.	Compounds	Observed C-S bond length in Å	SCF π-bond order	Calculated C-S bond length in Å from the linear relationship (I)
1.	paraffinic C-S bond (average value)	1.82 (7)	0.00	1.82
2.	1,4-dithiene	1.78 (8)	0.19 (9)	1.77
3. i	1,4-thiophthene	1.74 (10)	0.36 (11)	1.73
5.		1.72 (10)	0.41 (11)	1.71
4.	thiophene	1.74 (12)	0.34 (9)	1.73
6.	double C-S bond (average value)	1.56 (7)	1.00	1.56

The agreement between the calculated and observed values is quite good. Slight differences (of the order of 0.01 Å) are due to the fact that we have adopted the linear relationship while our curve shows a little curvature.

REFERENCES

1. C. A. Coulson, Proc. Roy. Soc. A 169, 413 (1939).
2. C. A. Coulson and A. Golebiewski, Proc. Phys. Soc. 78, 1310 (1961).
3. D. W. J. Cruickshank and R. A. Sparks, Proc. Roy. Soc. A 258, 270 (1960).
4. G. V. Boyd and N. Singer, Tetrahedron 22, 3383 (1966).
5. S. C. Abrahams, Quart. Rev. 10, 407 (1956).
6. A. Hordvik and E. Sletten, Acta Chem. Scand. 20, 1938 (1966).
7. Tables of Interatomic Distances, Special Publication No. 18, Chemical Society, London 1965.
8. P. A. Howell, R. M. Curtis, W. N. Lipscomb, Acta Cryst. 7, 498 (1954).
9. D. S. Sappenfield and M. Kreevoy, Tetrahedron 19 (Suppl. 2), 157 (1963).
10. M. G. Evans and J. de Heer, Acta Cryst. 2, 363 (1949).
11. N. Trinajstić and A. Hinchliffe, Croat. Chem. Acta 39, 119 (1967).
12. V. Schomaker and L. Pauling, J. Am. Chem. Soc. 61, 1769 (1939).