

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

A Theoretical Study of 1,4-Dithiadene by the L.C.A.O.-M.O. Method

BY MAURICE M. KREEVOY

RECEIVED MAY 3, 1958

1,4-Dithiadene (ref. 1) has been examined by the L.C.A.O.-M.O. method, neglecting overlap, σ - π -interaction and participation by the d-orbitals of sulfur. Semi-aromatic character is predicted with 28 kcal. per mole of resonance energy. Compared to benzene a very high basicity and great reactivity toward free radicals is indicated. The boat-like geometry of the molecule is correctly predicted. When the same methods are applied to thiophene and furan, fairly good agreement with experiment and with more elaborate calculations is obtained.

The interesting molecule 1,4-dithiadene (I) and several of its derivatives recently have been synthesized by Parham and his co-workers¹ and their chemistry has been examined. The parent compound is non-planar.² It has a high thermal stability but otherwise does not exhibit the reactions of an aromatic system.¹

The L.C.A.O.-M.O. method,³ neglecting overlap, has now been applied to I. As a sort of calibration, the same method also has been applied to thiophene, which already had been the subject of rather extensive experimental⁴ and theoretical^{5,6} investigation. In both molecules the distortion of bond angles from their preferred values was assumed to raise the energy of the molecule (lower the apparent resonance energy) by an amount proportional to the square of the distortion.⁷ The sulfur 3d-orbitals have been neglected.

In the case of thiophene the results compare quite well with those obtained from experiment and from the more elaborate calculations. For 1,4-dithiadene the results are in good agreement with the experimental facts insofar as these are known and some interesting predictions can be made. It is suggested that the differences between thiophene and furan are due principally to deformation of bond angles in the latter and changes in the Coulomb integral of the heteroatom, rather than to the sulfur 3d-orbitals as has previously been suggested.^{5,6}

Resonance Integrals.—Resonance integrals, H , have been estimated from the equation⁸

$$H_{ab} = H \frac{A_{ab}I_{ab}S_{ab}/(1 + S_{ab})}{ATS/(1 + S)} \quad (1)$$

where the quantities marked with the subscript ab refer to interactions between orbitals ψ_a and ψ_b and others refer to an aromatic carbon-carbon π -bond. Equation 1 is based on the assumption that the ex-

change integral is a nearly constant fraction of the bond energy.⁹ The parameters A were those of Mulliken⁹ and the mean ionization potentials, I , were assumed to be those of the atoms with the appropriate hybridization. Values of S , the overlap integral, were obtained for Slater atomic orbitals from the tables of Mulliken, Rieke, Orloff and Orloff.¹⁰

Coulomb Integrals.—The electronegativity of sulfur is the same as that of carbon.¹¹ The ionization potential for a sulfur 3p-orbital (10.36 volts) is not much different from that for a carbon 2p-orbital (11.26 volts),¹² and the ionization potential of hydrogen sulfide (10.47 volts) is virtually the same as that for ethylene (10.50 volts).¹³ Jaffé has estimated¹⁴ that the Coulomb integral for a sulfur 3p-orbital does not differ from that for a carbon 2p-orbital by more than 0.5β . The present author consequently follows Longuet-Higgins^{6a} and takes the Coulomb integral for sulfur equal to that for carbon in thiophene and 1,4-dithiadene.

The same arguments do not, however, apply to the Coulomb integral for an oxygen 2p-orbital, which undoubtedly has a more negative value than that of a carbon 2p-orbital.¹⁴

Thiophene.—The geometry of thiophene was assumed to be that given by Schomaker and Pauling.⁵ With these bond lengths the resonance integral given by eq. 1 for the sulfur 3p π -orbital with the C₂ (Fig. 1) 2p π -orbital is 0.94β , that for the 2p π -orbital of C₂ with the 2p π -orbital of C₃ is 1.06β , and that for the 2p π -orbital of C₃ with the 2p π -orbital of C₄ is 0.93β (where the resonance integral for the aromatic carbon-carbon π bond is β). The energy levels of the five-molecular π -orbitals were obtained in the usual way,³ and from these the coefficients of the atomic orbitals in each filled molecular orbital were evaluated. They are given in the Appendix.

With a carbon-carbon bond length of 1.35 \AA ,¹⁵ eq. 1 gives a resonance integral of 1.06β for the π -bond of ethylene and its delocalization energy is therefore 2.12β . The π -electron delocalization energy of thiophene, 6.30β , is obtained by summing over all the filled energy levels. The excess delocalization energy of thiophene over two ethylene molecules is 2.06β . Since β is thought to have a

(1) W. E. Parham, H. Wynberg, W. R. Hasek, P. A. Howell, R. N. Curtis and W. N. Lipscomb, *THIS JOURNAL*, **76**, 4957 (1954); other references may be found in this paper.

(2) P. A. Howell, R. M. Curtis and W. N. Lipscomb, *Acta Cryst.*, **7**, 498 (1954).

(3) C. A. Coulson, "Valence," Oxford at the Clarendon Press, 1952, p. 238.

(4) H. D. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952.

(5) V. Schomaker and L. Pauling, *THIS JOURNAL*, **61**, 1769 (1939).

(6) (a) H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949); (b) Joseph De Heer, *THIS JOURNAL*, **76**, 4802 (1954); (c) P. Daudel, R. Daudel, N. P. Buu-Hoi and M. Martin, *Bull. soc. chim. France*, 1202 (1948); (d) K. Kikuchi, *Science Reports of the Tohoku University*, **40**, 133 (1957); (e) K. Kikuchi, *ibid.*, **41**, 35 (1957).

(7) F. H. Westheimer, "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 523.

(8) M. Simonetta and S. Winstein, *THIS JOURNAL*, **76**, 18 (1954).

(9) R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

(10) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *ibid.*, **17**, 1248 (1949).

(11) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 64.

(12) United States Bureau of Standards, "Atomic Energy Levels," *Circ.* 467, Vol. 1, Table 23, p. XL (1948).

(13) W. C. Price, *Chem. Revs.*, **41**, 257 (1947).

(14) H. H. Jaffé, *J. Chem. Phys.*, **20**, 279 (1952).

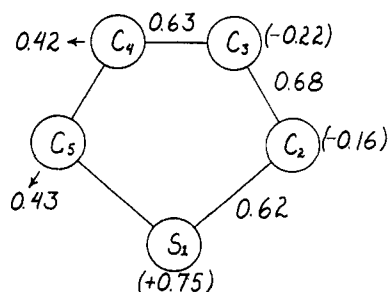


Fig. 1.—Thiophene: numbers in parentheses are charges in electronic units; numbers beside bonds are π -bond orders; arrows point to free valences.

value of around 18–20 kcal./mole, this would correspond to 37–41 kcal./mole.

In order to get a figure which is comparable with the experimental resonance energy of thiophene, the strain caused by distorting the preferred 120° ¹⁵ bond angles of ethylene to 112 – 113° ¹⁵ must be evaluated. This was done in the manner suggested by Westheimer⁷ using the appropriate bending force constant of ethylene given by Herzberg.¹⁶ The total strain obtained is ~ 3 kcal./mole so that the calculated resonance energy is 34–38 kcal./mole. This is in fairly good agreement with the empirical value 28–29 kcal./mole given by Wheland^{17,18} and obtained from heats of combustion.

Partial atomic charges, bond orders and free valences have been calculated in the usual way¹⁹ and are shown in Fig. 1. Table II compares the values for a number of molecules of interest. Included for comparison, also, are the values given by De Heer.^{6b} The present values lead to very much the same conclusions as those of De Heer and, in fact, are numerically almost indistinguishable from them except for the partial charges.

The present calculations show a partial negative charge on both the α - and β -carbon of thiophene, with the charge on the β -carbon being slightly larger than the charge on the α -carbon. The calculations of Longuet-Higgins and De Heer⁶ show no partial charges at all. The experimental fact is that thiophene is noticeably more reactive in electrophilic reactions than benzene, but the reactions take place at the α -rather than at the β -position.^{20,21}

(15) (a) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 439. (b) It has been pointed out by one of the referees that the spectroscopic data on ethylene referred to above are somewhat obsolescent, both in regard to the structure and the force constants. Use of the newer values (L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **27**, 1414 (1957); T. Shimanouchi, *ibid.*, **26**, 594 (1957)) would lower the calculated resonance energies of all three molecules under discussion, but it seems highly unlikely that the qualitative conclusions would be changed.

(16) Reference 15, p. 184.

(17) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 99.

(18) Other empirical values are of the same order of magnitude but differ somewhat in exact value. For example, Grosshof (H. Grosshof, *Chem. Ber.*, **84**, 916 (1951)) gives 24 kcal./mole while Pauling (L. Pauling, *ref. 11*, p. 226) gives 31 kcal./mole.

(19) Reference 3, pp. 238–254.

(20) H. D. Hartough, *J. Chem. Ed.*, **27**, 500 (1950).

(21) It seems quite likely that a better charge distribution, putting a larger negative charge on C_2 than on C_3 , would be obtained if a method involving a self-consistent field were used. Since the present method does not recognize charge separation as a source of potential energy, it does not show the preference of the electrons to be close to the positively charged sulfur atom.

In other respects both sets of results seem to be in general agreement with the experimental data.^{4,5}

Furan.—The same methods have been applied to furan to see if they would explain the difference between this molecule and thiophene.

The Coulomb integral for a $2p\pi$ -orbital of oxygen undoubtedly has a somewhat larger negative value than that for a $2p\pi$ -orbital of carbon.²² A value of about 0.5 β has been suggested for this difference by Jaffé¹⁴ and has been used successfully by Kreevoy and Taft²³ to calculate the resonance energies of conjugated carbonyl compounds; it also was used here.

Bak²⁴ and co-workers recently have reported a microwave study of furan which, together with some reasonable assumptions, sets the following limits on the bond lengths and bond angles (Numbering of the atoms follows that in Fig. 1): $1.337 \text{ \AA.} < R_{23} < 1.370 \text{ \AA.}$; $1.426 \text{ \AA.} < R_{34} < 1.458 \text{ \AA.}$; $1.356 \text{ \AA.} < R_{12} < 1.387 \text{ \AA.}$; $104^\circ 24' < \angle 512 < 107^\circ 30'$; $110^\circ 29' < \angle 123 < 111^\circ 43'$; $105^\circ 28' < \angle 234 < 106^\circ 34'$. The values $R_{34} = 1.44 \text{ \AA.}$ and $R_{23} = 1.35 \text{ \AA.}$ were used above for thiophene and are within these limits. They also were used for furan. Other values selected for furan are $R_{12} = 1.37 \text{ \AA.}$, $\angle 512 = 106^\circ$, $\angle 123 = 111^\circ$ and $\angle 234 = 106^\circ$. Using eq. 1 and Mulliken's tables¹⁰ a value of 0.755 β was obtained for the resonance integral of the C_2 $2p\pi$ -orbital with the oxygen $2p\pi$ -orbital. The carbon-carbon resonance integrals have been taken the same as for thiophene since the bond lengths are the same.

With these values of the integrals the calculated extra delocalization energy of furan is 1.80 β , 32–36 kcal./mole, depending on the value of β . The strain energy calculated from the bond angles given above is 6 kcal./mole^{15b}; therefore the calculated value to be compared with the experimental resonance energy is 26–30 kcal./mole, considerably lower than the comparable value for thiophene and in fair agreement with the empirical value of 17–22 kcal./mole given by Wheland.^{17,25}

The empirical resonance energy also may be reduced significantly through an inductive withdrawal of electrons from the carbon atoms by oxygen.²⁶ A reasonable σ^* for an ether oxygen can be obtained by multiplying 0.5 by 2.8, to get 1.4.²⁷ The standard substituents used by Wheland²⁵ would have σ^* essentially equal to zero. Since ρ^* for hydrogenation of olefins is 2.4, the heat of hydrogenation of furan is raised about 7 kcal./mole by inductive effects. (The oxygen is attached to unsaturated carbon atoms at two points.) If this 7 kcal./mole is subtracted from the 26–30 kcal./mole cited above, the result is in very good agreement indeed with the experimental value.

Inductive effects may also contribute to the difference between the calculated and observed resonance energies of thiophene.

(22) Reference 3, p. 242.

(23) M. M. Kreevoy and R. W. Taft, Jr., *THIS JOURNAL*, **79**, 4016 (1957).

(24) B. Bak, L. Hansen and J. Rastrup-Andersen, *Faraday Soc. Discussions*, **19**, 30 (1955).

(25) Reference 17, p. 99, p. 85.

(26) R. W. Taft and M. M. Kreevoy, *THIS JOURNAL*, **79**, 4011 (1957).

(27) R. W. Taft, Jr., *ref. 7*, p. 605.

It is interesting to note the important role played by strain arising from the deformation of the ethylenic bond angles in furan. The effect appears in two forms: the strain energy in furan is twice that in thiophene, which significantly lowers the apparent resonance energy; the oxygen-carbon distance is increased so that the oxygen-carbon π -bond in furan is weaker than the sulfur-carbon π -bond in thiophene.^{15b}

1,4-Dithiadene.—Since the present methods give fairly acceptable results when applied to thiophene, they will now be applied to 1,4-dithiadene, Fig. 2, a less understood molecule.

Symmetry considerations give these trial functions for 1,4-dithiadene²³ (the molecule has a boat-like shape and C_{2v} symmetry²)

$$\left. \begin{aligned} \psi_a &= \frac{1}{2} (\psi_1 + \psi_4) \\ \psi_b &= \frac{1}{4} (\psi_2 + \psi_5 + \psi_3 + \psi_6) \\ \psi_c &= \frac{1}{4} (\psi_2 + \psi_5 - \psi_3 - \psi_6) = \Psi_3 \\ \psi_d &= \frac{1}{4} (\psi_2 - \psi_5 + \psi_3 - \psi_6) = \Psi_4 \\ \psi_e &= \frac{1}{2} (\psi_1 - \psi_4) \\ \psi_f &= \frac{1}{4} (\psi_2 - \psi_5 - \psi_3 + \psi_6) \end{aligned} \right\} \begin{array}{l} \Psi_1 \text{ and } \Psi_2 \\ \Psi_5 \text{ and } \Psi_6 \end{array}$$

Final molecular wave functions are Ψ_n ; ψ_x are symmetry functions and ψ_n are Slater atomic p-orbitals. As indicated, ψ_c and ψ_d are already final molecular orbitals: ψ_a and ψ_b were combined by the variation method to give Ψ_1 and Ψ_2 ; in a similar manner ψ_e and ψ_f give Ψ_5 and Ψ_6 . If the Coulomb integral of the sulfur 3p π -orbital is assumed equal to that of the carbon 2p π -orbital, these various energy levels are obtained.

$$\left. \begin{aligned} E_1 &= \frac{H_{23} + \sqrt{H_{23}^2 + 8H_{12}^2}}{2} \\ E_2 &= \frac{H_{23} - \sqrt{H_{23}^2 + 8H_{12}^2}}{2} \\ E_3 &= -H_{23} \\ E_4 &= +H_{23} \\ E_5 &= \frac{-H_{23} + \sqrt{H_{23}^2 + 8H_{12}^2}}{2} \\ E_6 &= \frac{-H_{23} - \sqrt{H_{23}^2 + 8H_{12}^2}}{2} \end{aligned} \right\} \quad (2)$$

With 8 π -electrons to be accommodated, Ψ_1 , Ψ_2 , Ψ_4 and Ψ_5 will each be doubly occupied in the lowest energy state of the molecule if $H_{12} < H_{23}$ (it is shown in Table I that this is the case). The total π -electron delocalization energy is, then, given by eq. 3.

$$E = 3H_{23} + \sqrt{H_{23}^2 + 8H_{12}^2} \quad (3)$$

If it is assumed that the bond lengths in 1,4-dithiadene are fixed, H_{23} is not a function of the angle α ; H_{12} is, however. For maximum overlap the sulfur 3p π -orbital and the adjacent carbon 2p π -orbital should have a common nodal plane.

(28) H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 384.

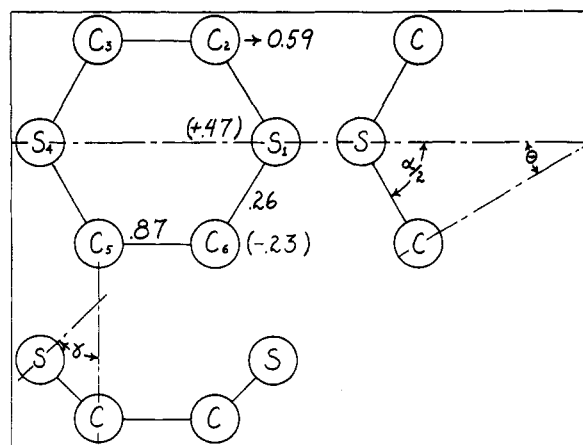


Fig. 2.—1,4-Dithiadene: numbers in parentheses are charges in electronic units. Numbers beside bonds are π -bond orders. Arrows point to free valences.

To achieve this the carbon-sulfur-carbon angle would have to be enlarged from its preferred value of around 90° ²⁹ to around 120° . In practice a compromise is effected,² with the carbon-sulfur-carbon angle somewhat enlarged, the carbon-carbon-sulfur angle likewise somewhat enlarged (both leading to some strain) and the angle α reduced from 180° (with a consequent loss in delocalization energy). If it is assumed that the σ -bond energy is given by a constant, E_σ , and the strain energy is given by E_s , the total energy of the molecule will be

$$E = E_\pi + E_s + E_\sigma \quad (4)$$

where E_π and E_s are functions of α and E_σ is not. The angle α then can be found by minimizing E . In the present work this was done by trial and error.

The bond lengths were assumed to be 1.78 Å. for the carbon-sulfur bond,² and 1.35 Å. for the carbon-carbon bond.³⁰ The carbon-carbon-sulfur angle was assumed to have a fixed value of 125° .² Equation 1 gives 1.06β for the resonance integral of the carbon-carbon π -bond, H_{23} . In order to calculate the resonance integral for the carbon-sulfur π -bond from eq. 1 the overlap integral taken from Mulliken's tables¹⁰ must be multiplied by the cosine of the angle θ and the cosine of the angle γ (Fig. 2). Equation 5 gives θ in terms of α and eq. 6 gives γ in terms of α and the assumed bond lengths.

$$\theta = 90^\circ - (\alpha/2) \quad (5)$$

$$\tan \gamma = 1.48 \cos(\alpha/2) \quad (6)$$

For calculating strain, the carbon-sulfur-carbon angle also is needed as a function of α and it is given by

$$\cos(1/2 \angle \text{CSC}) = \frac{\sqrt{1.04 + 2.28 \cos^2(\alpha/2)}}{1.78} \quad (7)$$

From eqs. 1, 3, 5 and 6, E_π was calculated for $\alpha = 120^\circ$, 180° and intermediate values. For the

(29) L. Pauling, ref. 11, Chapt. III.

(30) Lipscomb and co-workers (ref. 2) give 1.29 Å. for the carbon-carbon bond distance, but they indicate that a large uncertainty is associated with this value. Since it is considerably shorter than the normal carbon-carbon double bond length, it seems unlikely that it is correct, and the carbon-carbon bond distance of ethylene was used instead (ref. 15).

strain energies due to deforming the carbon-sulfur-carbon angle, Westheimer's method was used with the force constant that for H_2S .²⁹ The unstrained bond angle was assumed to be 92° , as in H_2S .³¹ Since the carbon-carbon-sulfur angle was assumed to have a fixed value of 125° , strain due to this source is not a function of α , and represents a constant factor in E_s (1.3 kcal./mole).^{15b} Strain energies (positive) and delocalization energies (negative) are shown in Table I. To get the values shown in Table I, β was assigned the value 18 kcal./mole.³

TABLE I

α	ENERGY AS A FUNCTION OF α			$\angle CSC$
	H_{12}^b	E_{π^a}	$E_s + E_{\pi^a}$	
180	0.94 β	-110.2	-97.6	110°
160	.90 β	-109.1	-98.9	108°
140	.81 β	-106.9	-103.4	100°
136	.79 β	-106.3	-103.8	98°
134	.78 β	-106.1	-103.9	97°
132	.77 β	-105.8	-104.0	96°
130	.76 β	-105.5	-103.9	95°
124	.72 β	-104.3	-103.1	92°
120	.69 β	-103.7	-102.3	90°

^a Kcal./mole. ^b Since H_{23} has a value of 1.06 β all of the values of H_{12} are smaller than H_{23} , as is required if eq. 3 is to hold.

From Table I the predicted angle α is 132° and the predicted carbon-sulfur-carbon angle is 96° , in excellent agreement with the experimental values of $137 \pm 2^\circ$ or $141 \pm 2^\circ$ and $100 \pm 2^\circ$ or $102 \pm 2^\circ$.^{2,32}

From Table I it can also be predicted that the barrier to turning the "boat" inside-out should be 6.4 kcal./mole, a prediction that might be tested spectroscopically or calorimetrically. By subtracting 76.3, the calculated total delocalization energy of two ethylene molecules, from 104.0, a resonance energy of 28 kcal./mole can be predicted. This value is intermediate between the resonance energy predicted for thiophene and that predicted for furan, which might be expected to lead to an "aromaticity" intermediate between that of thiophene and that of furan. This is in fair agreement with the facts as they are known.¹ The resonance energy predicted above could be too low because of neglected d-orbital and $\sigma-\pi$ interactions. (Unlike thiophene and furan, the present molecule is not planar, so that the classification of orbitals into σ and π is not strictly legitimate.) On the other hand, the resonance energies calculated for thiophene and furan in the same way are both slightly higher than the best estimated empirical values. The calculated value might be tested by measuring the heat of combustion of 1,4-dithiadene or its heat of hydrogenation.

The energy levels appropriate to $\alpha = 132^\circ$ and the coefficients of the atomic orbitals in each filled molecular orbital are tabulated in the Appendix. These lead to the atomic charges, bond orders and

(31) Reference 15a, p. 161.

(32) It is probably of no great significance, in view of the uncertainties in the calculations, but the calculated values are in better agreement with "model A" than "model B" (ref. 2, lower values). Lipscomb and co-workers (ref. 2) also favor "model A" slightly on the basis of the experimental data.

free valences shown in Fig. 2. The most unusual aspect of all these is the fact that two of the electrons in 1,4-dithiadene are in an antibonding orbital. This indicates that the ionization potential of 1,4-dithiadene should be considerably less than that of a related compound such as thiophene. As a corollary it suggests that 1,4-dithiadene should be quite susceptible to oxidation, which is in accord with the facts.¹ It also suggests susceptibility to attack by electrophilic reagents.

The bond orders are not inconsistent with the experimental bond lengths,² within the considerable uncertainty of the latter. The carbon-sulfur bond has less double-bond character than that in thiophene, which is consistent with its length—intermediate between that of thiophene and the "normal" carbon-sulfur bond length. The shortening of the carbon-carbon bond length beyond the value for a "normal" carbon-carbon double bond may be experimental uncertainty. On the other hand, it may be characteristic of resonance-stabilized systems having nearly full double-bond character.

The partial negative charge on carbon is larger than that calculated for thiophene which reinforces the suggestion of susceptibility to attack by electrophilic reagents. The free valence of the carbon is greater than that for benzene or thiophene (although it does not approach that of ethylene or butadiene) which suggests susceptibility to attack by free radicals. It also suggests a somewhat smaller "aromatic character" for 1,4-dithiadene than for thiophene. Partial charges, bond orders and free valences are collected in Table II.

TABLE II

Compound and atom or bond	Partial charge, electronic units	Free valence	Mobile bond order
Benzene	0.00	0.40	0.67
Ethylene	0.00	0.73	1.00
S^a	0.00, ^c +0.75 ^d		
C_2^a	.00, ^c -.16 ^d	0.37, ^c 0.42 ^d	
C_3^a	.00, ^c -.22 ^d	.34, ^c .43 ^d	
$S-C_2^a$			0.62 ^d
$C_2-C_3^a$.68 ^d
$C_2-C_4^a$.63 ^d
S^b	+0.47		
C^b	-0.23	0.59	
$S-C^b$.256
$C-C^b$.873

^a Thiophene. ^b 1,4-dithiadene. ^c Taken from ref. 6b. ^d Present work.

Localization Energies.—Coulson³³ and Szwarc and Leavitt³⁴ have shown that there is a linear relationship between the log of the methyl affinity³⁵ of an unsaturated hydrocarbon and its localization energy. The localization energy is defined as the loss in resonance energy on formation of a σ -bond at one of the carbon atoms by a free radical.³³ It was also pointed out that there was a correlation between methyl affinities and free valences.³³ It follows, of course, that there is, in general, a linear correlation between free valences and localization energies. While these relationships have not been

(33) C. A. Coulson, *J. Chem. Soc.*, 1435 (1955).

(34) M. Szwarc and F. Leavitt, *This Journal*, **78**, 3590 (1956).

(35) M. Levy and M. Szwarc, *J. Chem. Phys.*, **22**, 1621 (1954).

Appendix

ENERGY LEVELS AND COEFFICIENTS OF ATOMIC ORBITALS FOR MOLECULAR ORBITALS OF THIOPHENE AND 1,4-DITHIADIENE

	E	C_1	C_2	C_3	C_4	C_5	C_6
Thiophene							
1	+1.930 β	0.428	0.439	0.465	0.465	0.439	
2	+0.531 β	.663	.187	-.496	-.496	.187	
3	-1.571 β						
4	+0.691 β	.000	.593	.386	-.386	-.593	
5	-1.621 β						
1,4-dithiadiene							
1	+1.88 β	0.354	0.432	0.432	0.354	0.432	0.432
2	-0.82 β	.564	-.300	-.300	.564	-.300	-.300
3	-1.06 β						
4	+1.06 β	.000	+.500	+.500	.000	-.500	-.500
5	+0.82 β	+.564	+.300	-.300	-.564	-.300	+.300
6	-1.88 β						

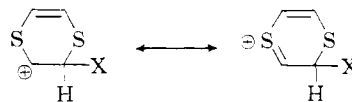
quantitatively applied to heterocyclic compounds, it has been indicated that these should not differ too much from related hydrocarbons.³³

The free valence and localization energy of thiophene fit in with the above generalizations nicely, the localization energy (2.45 β) being a bit smaller than that for benzene (2.54 β) while the free valence (0.43) is a bit larger. In calculating the resonance energy of thiophene after attack by a radical, the resonance integral was assumed to be 1.00 β for all adjacent atoms since the exact geometry is unknown. For the same reason strain was assumed to be the same as in the parent molecule. Unfortunately the methyl affinity of thiophene does not seem to be known, but the calculations give no reason to think that it would be other than slightly higher than that for benzene.

The same thing is not true for 1,4-dithiadiene. While the free valence for the carbon atoms of this compound is intermediate between those of benzene and those of ethylene, its localization energy (1.42 β) is much less than either. The approximations as to geometry and resonance integrals were the same as those mentioned for thiophene, causing some uncertainty as to the exact value of localization energy, but it is so much lower than that of any compound previously studied that the qualitative prediction cannot be altered in any reasonable way. If the

linear relation between the log of the methyl affinities and the localization energies holds, the methyl affinity of 1,4-dithiadiene should be 10^7 times that of benzene!

Even more striking is the small loss in resonance energy calculated for 1,4-dithiadiene when it reacts with a positively charged species. The resultant ion has a calculated resonance energy only 0.42 β less than that of the parent compound.



The same approximations for resonance integrals and strain mentioned above are involved here, but no reasonable set of approximations can bring the value even close to the 2.53 β calculated loss of resonance energy for benzene in a similar process or the 2.00 β for ethylene or even the 1.83 β calculated loss for thiophene. The comparatively tiny calculated loss for 1,4-dithiadiene indicates that this compound should be *much* more basic than benzene or thiophene. It also strongly suggests that 1,4-dithiadiene should be very susceptible to attack by electrophilic reagents.

MINNEAPOLIS 14, MINN.

[CONTRIBUTION FROM THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION]

Triazines. XXI. The Preparation of *s*-Triazine Aldehydes^{1,2}

BY EHRENFRIED KOBER AND CHRISTOPH GRUNDMANN

RECEIVED MARCH 11, 1958

Several hydrazones of 4,6-disubstituted *s*-triazine aldehydes were obtained by reduction of the corresponding 4,6-disubstituted 2-diazomethyl-*s*-triazines with hydrogen sulfide or alkylthiols. These hydrazones could be cleaved to the free *s*-triazine aldehydes. The properties of two of these aldehydes are described. A number of unsuccessful attempts to prepare *s*-triazine aldehydes by conventional routes are discussed briefly.

Although much work has been done in the last years in the *s*-triazine series, *s*-triazine aldehydes are

(1) This article is based on work performed under project 116-B of The Ohio State University Research Foundation sponsored by the Olin Mathieson Chemical Corporation, New York, N. Y.

(2) Preceding communication: Ch. Grundmann and A. Kreutzberger, *THIS JOURNAL*, **80**, in press (1958).

still unknown. Oximes of substituted tetrahydro-*s*-triazine aldehydes have been prepared, but not the free aldehydes.³ Likewise, attempts to hydrolyze

(3) A. Ostrogovich and V. Crasu, *Gazz. chim. ital.*, **64**, 800 (1934); **66**, 653 (1936); A. Ostrogovich and J. Cadariu, *ibid.*, **71**, 505, 515, 524 (1941).