# Structural and Spectroscopic Studies of 2,5-Dithiahex-3-yne

BY BRIAN BEAGLEY AND VERA ULBRECHT

Department of Chemistry, University of Manchester Institute of Science
and Technology, Manchester M60 1QD

SHUNJI KATSUMATA† AND D. ROBERT LLOYD

Department of Chemistry, University of Birmingham, Birmingham B15 2TT

JOSEPH A. CONNOR* AND GERALD A. HUDSON

Department of Chemistry, University of Manchester, Manchester M13 9PL

*Received* 6*th December*, 1976

The structure of 2,5-dithiahex-3-yne, $CH_3SC{\equiv}CSCH_3$, has been determined by electron diffraction in the gas phase to give (on the $r_a$-basis, and with e.s.d.) $r$(S—C≡) 1.671(2) Å, $r$(S—$CH_3$) 1.806(2) Å, ∠CSC 102.7(2)° with the dihedral (torsion) angle $\phi$(CSSC) $86 \pm 5°$. The gas photoelectron spectra (He I and He II) have been measured and interpreted with the aid of CNDO/2 molecular orbital calculations. The i.r., Raman, n.m.r. ($^1$H and $^{13}$C) and u.v./visible spectra have also been recorded. The results of these various measurements are used to show that there is no definite evidence of conjugation between the sulphur atoms and the acetylenic triple bond.

In the course of a study of the coordination chemistry of 2,5-dithiahex-3-yne,[1] we were interested in determining whether there was evidence for interaction ($\pi$-bonding) between the acetylenic triple bond and the sulphur lone pairs. The existence of such $\pi$-bonding might be expected to influence the type of bond formed with a transition metal insofar as the donor/acceptor character of the two sites would change. The results of a structural and spectroscopic study which we report are of interest in relation to other hetero-substituted alkynes, especially alkynyl phosphines which can coordinate a metal atom by either or both of the potential donor sites.[2]

## EXPERIMENTAL

The acetylene, 2,5-dithiahex-3-yne was obtained as a colourless liquid (b.p. 345 K/10 Torr) from the reaction between sodium acetylide and methylthiocyanate in liquid ammonia at 195 K as described [29] by Brandsma.

Analysis: Found C 40.5, H 5.0, S 54.3; $C_4H_6S_2$ requires C 40.7, H 5.1, S 54.3 %. On standing the liquid acquired a pale yellow colour which deepened on exposure to sunlight and to air. Redistillation removed this impurity, which was not characterised.

The gas phase electron diffraction pattern was recorded in the Balzers KDG2 electron diffraction instrument [30] in experiments using camera distances of nominally 100, 50 and 25 cm. The sample issued from the internal reservoir of the gas nozzle at a temperature of 358 K maintained by a circulating flow of hot water. Diffraction rings were observed to extend to $s \sim 30$ Å$^{-1}$. Three good photographic plates from each experiment were selected for microdensitometry using the Joyce Loebl Mk3 Autodensidator. The total numbers of

---

† Permanent address: Laboratory of Physical Chemistry, Institute of Applied Electricity, Hokkaido University, Sapporo, Japan.

pattern diameters automatically scanned were 11, 9 and 12 respectively, for the three camera distances. The microdensitometer data were processed by routine methods,[31] and the radial distribution curve (fig. 1) was obtained.

Measurements of the He I and He II photoelectron spectra were carried out with a Perkin-Elmer PS18 spectrometer described elsewhere.[32] The He I spectrum was calibrated from the sharp bands of $CH_3I$ and Ar as internal standards. The resolution of the instrument at the Ar band maxima was 19 and 140 meV for He I and He II excitation respectively.

Infrared spectra were recorded with Perkin-Elmer 225 and 257 grating spectrometers using thin films of the liquid acetylene between sodium chloride, calcium fluoride or caesium iodide plates as appropriate. Raman spectra were recorded with a Cary 82 spectrometer. The spectra were calibrated with reference to water and $CCl_4$. Nuclear magnetic resonance spectra were recorded on a Varian XL100 instrument and referenced to TMS. U.v./visible spectra were recorded with a Unicam SP800 instrument.

## RESULTS AND DISCUSSION

### STRUCTURE OF 2,5-DITHIAHEX-3-YNE BY ELECTRON DIFFRACTION

The peaks on the radial distribution curve (fig. 1) may be assigned as follows: C—H and C≡C unresolved at 1.1-1.2 Å, $S—CH_3$ and S—C≡ unresolved in the 1.75 Å peak, S...H in the plateau at 2.4-2.6 Å, $\equiv C...CH_3$ and C≡...S at 2.9 Å, $C\equiv...CH_3$ in the broad low peak at 3.5-3.9 Å, S...S at 4.55 Å, and $S...CH_3$ in the broad peak at 5.0-5.5 Å. There is also a very low broad peak centred at 6.2 Å, which may be tentatively assigned to $H_3C...CH_3$. There is no prominent feature which can be assigned to a distance X...H (such as ≡C...H) which will fix the orientation of the methyl hydrogen atoms; furthermore, the peaks (involving the methyl group) which fix $\angle \equiv CSCH_3$ are either unresolved or broad and diffuse. The general features of the molecule which are uncertain after inspection of the r.d. curve are clearly those fixing the orientation of the methyl groups and their hydrogen atoms with respect to the rest of the molecule.

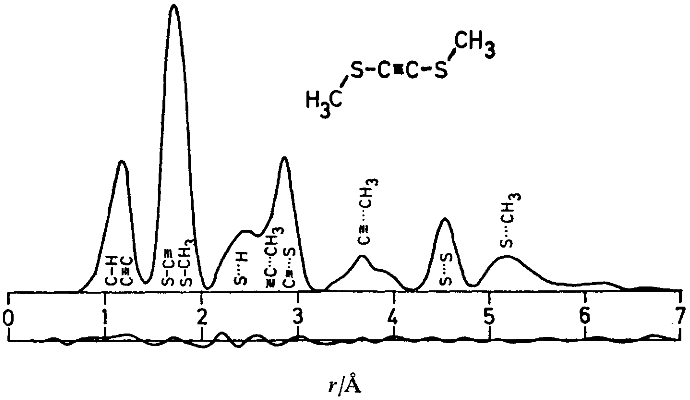

FIG. 1.—2,5-Dithiahex-3-yne. Final and difference radial distribution curves. Damping constant, 0.002 Å$^2$.

The model adopted for use in least-squares refinements of the geometry was based on the assumptions (i) that the S—C≡C—S spine of the molecule is linear and (ii) that the methyl hydrogen atoms are staggered with respect to the spine. The second assumption was tested during the series of refinements. The chosen independent geometrical parameters defining atomic positions in this model are C—H, C≡C, S—C≡, S—CH$_3$, ∠SCH, ∠CSC and the dihedral angle, $\phi_{CS-SC}$, which fixes the mutual orientation of the methyl groups. In addition, shrinkages [3] for distances C≡...S and S...S were treated as variable parameters.

The first series of least-squares refinements, based on molecular intensity curves derived with optimised background functions, led to the results shown in column I of table 1. It proved impossible to refine convergently the amplitudes of the X...H distances which depend on the orientation of the methyl-group hydrogen atoms; these amplitudes were fixed temporarily at 0.3 Å, a value large enough to reduce the systematic errors which would occur if assumption (ii) were incorrect. No information about the H$_3$C...CH$_3$ distance could be obtained in refinement I. Disturbing geometrical features from refinement I are the short C≡C bond of 1.200±0.004 Å (acetylene has [4] $r_a$ = 1.211 Å) and the negative shrinkages; also, perhaps ∠CSC is unexpectedly large. The correlation matrix for refinement I showed considerable correlation between the shrinkages and the bond lengths, as well as between the bond lengths themselves.

TABLE 1.—RESULTS FROM LEAST-SQUARES REFINEMENTS USING ELECTRON DIFFRACTION DATA FOR $CH_3SC{\equiv}CSCH_3$

(distances and amplitudes in Å, angles in degrees)

independent geometrical parameters ($r_a$ basis)

| | I | II | III (preferred) | e.s.d. |
|---|---|---|---|---|
| C—H | 1.09 [a] | 1.09 [a] | 1.09 [a] | — |
| C≡C | 1.200 | 1.211 [a] | 1.211 [a] | — |
| S—C≡ | 1.671 | 1.671 | 1.671 | 0.002 |
| S—CH$_3$ | 1.804 | 1.806 | 1.806 | 0.002 |
| ∠SCH | 109.6 | 109.4 | 109.3 | 0.3 |
| ∠CSC | 103.2 | 103.1 | 102.7 | 0.2 |
| shrinkages: | | | | |
| C≡...S | −0.008 | 0.004 | −0.001 | 0.004 |
| S...S | −0.001 | 0.010 | 0.012 | 0.004 |
| $\phi_{CSSC}$ | — | — | 86 | 5 |
| residual (%), $R$ | 6.22 | 6.44 | 6.14 | — |

amplitudes and dependent distances

| | distances | amplitude I | amplitude II | amplitude III | |
|---|---|---|---|---|---|
| C—H | | 0.078 [a] | 0.078 [a] | 0.078 [a] | — |
| C≡C | | 0.008 | 0.012 | 0.011 | 0.010 |
| S—C≡ | | 0.054 | 0.054 | 0.053 | 0.004 |
| S—CH$_3$ | | 0.054 | 0.056 | 0.055 | 0.004 |
| C≡...S | 2.88 | 0.062 | 0.064 | 0.060 | 0.004 |
| ≡C...CH$_3$ | 2.72 | 0.114 | 0.117 | 0.101 | 0.010 |
| S...H | 2.40 | 0.095 | 0.096 | 0.094 | 0.006 |
| S...S | 4.54 | 0.071 | 0.073 | 0.075 | 0.004 |
| C≡...CH$_3$ | 3.72 | 0.158 | 0.158 | 0.161 | 0.011 |
| S...CH$_3$ | 5.24 | 0.193 | 0.193 | 0.174 | 0.010 |
| H...H | 1.79 | 0.12 [a] | 0.12 [a] | 0.12 [a] | — |
| H$_3$C...CH$_3$ | 5.85 | 0.30 [a] | 0.30 [a] | 0.32 | 0.04 |
| X...H | [b] | 0.30 [a] | 0.30 [a] | [b] | — |

[a] Parameter fixed during refinement. [b] See table 2.

The negative shrinkages were regarded as unacceptable results. The various correlations with the shrinkages were studied in a second series of refinements; it was soon evident that the shrinkage values depend critically on the value adopted for the length of the triple bond. Indeed, the shrinkages moved positive and then slowly increased in value as $C\equiv C$ was increased in length. The refinement with $C\equiv C = 1.211$ Å (the acetylene value) was considered as the most reasonable one, and its results are given in column II of table 1. A refinement with $\angle$CSC fixed at 100° gave a poor fit between observed and calculated data ($R = 9.5$ %), showing beyond doubt that the largish $\angle$CSC angle obtained by refinement is reasonable.

The molecular features as yet unestablished were those fixing the orientation of the methyl groups and their hydrogen atoms with respect to the rest of the molecule. Refinements in which the methyl hydrogen atoms are eclipsed with respect to the spine of the molecule gave a residual $>2$ % higher than corresponding ones with staggering assumed. Assumption (ii) was, therefore, retained and attempts were again made to refine the amplitudes of the orientation-dependent X...H distances. Refining all these amplitudes independently again proved unsatisfactory, and a simple model relating them was adopted. For a given spine atom, X, the staggered form has two short X...H distances and one longer one. Studies [5] of related systems have shown that X...H(short) has a *larger* amplitude than X...H(long), often by as much as a factor, $k$, of two; this is because of the different magnitudes of $\partial R/\partial\phi$, the rate of change of an X...H distance with torsional oscillation of a methyl group around the S—$CH_3$ bond. The amplitude of X...H(long) was fixed slightly larger than the refined value of the corresponding amplitudes for X...$CH_3$, and the factor $k$ was optimised. The value $k = 2.5$ gave the lowest residual; the corresponding results are in column III of table 1. The optimised model for these amplitudes is presented in table 2 which also gives the values of the distances involved.

TABLE 2.—AMPLITUDE MODEL FOR METHYL TORSION
(distances and amplitudes in Å)

| X | | X···$CH_3$ | X···H(long) | X···H(short) |
|---|---|---|---|---|
| ≡C | $r_a$ | 2.72 | 3.68 | 2.91 |
| | $u$ | 0.101 | 0.12 | 0.30 |
| C≡ | $r_a$ | 3.72 | 4.76 | 3.73 |
| | $u$ | 0.161 | 0.18 | 0.45 |
| S | $r_a$ | 5.24 | 6.31 | 5.11 |
| | $u$ | 0.174 | 0.18 | 0.45 |

It was noted during the series of refinements culminating in the results of column III of table 1 that both the torsion angle $\phi_{CSSC}$ and the amplitude of $H_3C...CH_3$ would now refine convergently. These refined values are given in column III, and were obtained regardless of the initial value of $\phi_{CSSC}$ in the range 0-180°. As a consequence of establishing the $H_3C...CH_3$ distance to be $\sim$5.85 Å, the earlier tentative assignment of the 6.2 Å feature on the r.d. curve must be revised; the 6.2 Å feature must represent S...H(long).

Several alternative amplitude models for the X...H distances were investigated. None gave a residual as low as that in column III of table 1. However, it became clear that the $H_3C...CH_3$ distance (and hence $\phi_{CSSC}$) is highly correlated with the amplitude of S...H(long); values for $H_3C...CH_3$ distances of 5.85-6.22 Å ($\phi_{CSSC}$ = 85-130°) were obtained for amplitudes of S...H(long) in the range 0.18-0.50 Å. As the previous optimization of the amplitudes rules out values greater than $\sim$0.25 Å for the amplitude of S...H(long), the larger values of $\phi_{CSSC}$ are unsatisfactory and an e.s.d. of ±5° reasonably expresses the uncertainty of $\phi_{CSSC}$ including errors in the amplitude model.

Finally, the effect of fixing the amplitude of C≡C at 0.035 Å (the value observed[4] in $H_3CC{\equiv}CCH_3$), and the effect of allowing the C—H distance to refine, were tested. There were no significant changes in parameters, nor in residuals, in either case; the C—H distance refined to 1.089±0.004 Å.

The final column of table 1 gives the estimated standard deviations (e.s.d.) of the parameters of refinement III. The values given were obtained by upward correction of the diagonal least-squares e.s.d. to take account of correlation between data points, errors due to other experimental and computational factors, errors in the choice of model and errors in the electron wavelength (0.056 75±0.000 02 Å). Final experimental and difference radial distribution curves are shown in fig. 1.

The lower residual of refinement III, compared with II, lends confidence to the preference for a staggered arrangement of the methyl hydrogen atoms with respect to the spine of the molecule. Although the best fit of the model to the experimental data also gave a specific value of $\phi_{CSSC}$, it is not necessarily correct to conclude from the diffraction data alone (but see section below) that the molecule has a preferred conformation about the SC≡CS spine. The $H_3C...CH_3$ distance changes from 5.3-6.4 Å for a change in $\phi_{CSSC}$ of 0-180°. The refined value of 5.85 Å is midway between these extremes, and may simply represent the best attempt to fit a single distance to a smear of radial distribution representing free rotation.

As the (C≡C) bond length is a fixed parameter in the refinement of the structure, we confine our attention to the values obtained for other distances and angles for comparison with other molecules. The ($S—CH_3$) bond length in $(MeS)_2C_2$ ($r_a$ 1.806 Å) is the same as that found[5] in $Me_2S_2$ ($r_a$ 1.806 Å) and[6] in $MeSCH{=}CH_2$ ($r_a$ 1.806 Å); it is similar to that[7] in MeSC≡CH ($r_a$ 1.814 Å) and[8] in MeSCN ($r_s$ 1.837; $r_0$ 1.806 Å). The [S—C(*sp*)] bond length in $(MeS)_2C_2$ ($r_a$ 1.671 Å) is again closely comparable with that[7] in MeSC≡CH ($r_a$ 1.682 Å) and[8] in MeSCN ($r_s$ 1.684 Å; $r_0$ 1.697 Å).

An estimate of the C(*sp*) radius can be obtained by subtraction of the C($sp^3$) radius (0.767 Å) in ethane[11] from the $CH_3$—C bond length in but-2-yne[10] ($r_g$ 1.467 Å), giving 0.700 Å. Addition of this to the radius of S(II) [1.041 Å in[5] $(CH_3)_2S_2$] gives an estimated pure single bond length C(*sp*)—S(II) of 1.741 Å, which is appreciably longer (0.070 Å) than the measured distance in 2,5-dithiahex-3-yne. However, many recent studies have shown[9] that the [C($sp^3$)—S(II)] bond length varies over the range 1.80-1.86 Å, suggesting that the S(II) radius is very variable. Thus the apparent shortening of the [C(*sp*)—S(II)] distance by 0.070 Å in 2,5-dithiahex-3-yne might not be very significant. Comparing S—C distances within the molecule shows a difference of 0.135 Å between $CH_3$—S and S—C≡. The difference between the radii of C($sp^3$) and C(*sp*) estimated above is only 0.067 Å, which suggests that there may be a genuine shortening of the S—C≡ bond, though it may not be due to delocalisation; there is certainly no accompanying lengthening of the C≡C bond.

## ULTRAVIOLET PHOTOELECTRON SPECTRA OF 2,5-DITHIAHEX-3-YNE

The He I and He II photoelectron spectra are shown in fig. 2. Three well-defined bands A, B and C are observed in the 8-13 eV region, and a broad feature D with at least three components is found at higher i.p. Distinct splittings are visible on A and B, and C has a slightly irregular outline.

The photoelectron spectra have been analysed with the help of both CNDO/2 calculations[12] and the variation of differential photoionisation cross-sections with

He I and He II radiation.[13] The CNDO/2 calculations of $(MeS)_2C_2$ were carried out for various dihedral angles, $\phi$, from 0-180° at intervals of 15° using the experimental bond lengths and angles of table 1. The experimental vertical i.p. values, and the

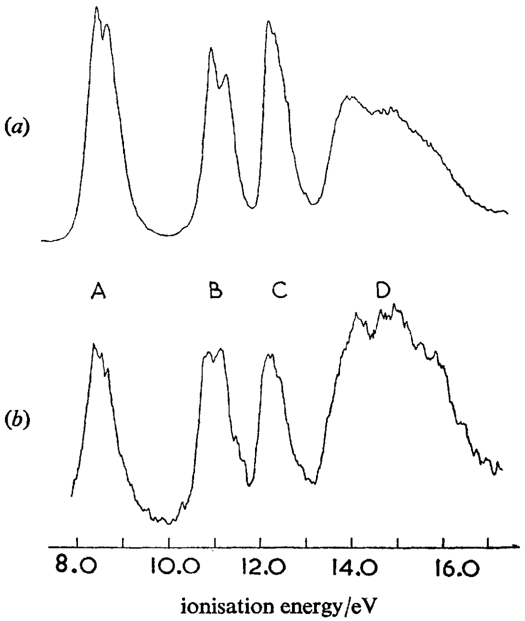

FIG. 2.—Ultraviolet photoelectron spectra of 2,5-dithiahex-3-yne excited by (*a*) He I (21.2 eV) and (*b*) He II (40.8 eV) radiation.

TABLE 3

(*a*) EXPERIMENTAL VERTICAL IONIZATION ENERGIES FOR $CH_3SC{\equiv}CSCH_3$

| band | vertical I.E./eV | assignment |
|---|---|---|
| A | 8.41 | 8*b* |
| | 8.64 | 9*a* |
| B | 10.94 | 6*b* |
| | 11.25 | 6*a* |
| C | 12.19 | 8*a*, 7*b* |
| D | 14.1 | 7*a*, 5*b* |
| | 14.9-15.9 | 5*a*, 4*b*, 4*a*, 3*b* |

(*b*) CNDO/2 EIGENVALUES FOR $CH_3SC{\equiv}CSCH_3$

| m.o. energy/eV | symmetry | character | sulphur 3*p* population |
|---|---|---|---|
| −11.05 | 8*b* | $n_s^+$ | 0.64 |
| −11.18 | 9*a* | $n_s^-$ | 0.63 |
| −14.26 | 8*a* | $\sigma_s^+$ | 0.50 |
| −14.70 | 7*b* | $\sigma_s^-$ | 0.47 |
| −15.51 | 7*a* | S—C...C—S$^+$ | 0.31 |
| −17.05 | 6*b* | $\pi_{C\equiv C}$ | 0.19 |
| −18.15 | 6*a* | $\pi_{C\equiv C}$ | 0.24 |
| −19.03 | 5*b* | S—C...C—S$^-$ | 0.22 |
| −20.93 | 5*a* | $\pi_{\overset{+}{C}H_3}$ | 0.07 |
| −20.99 | 4*b* | $\pi_{\overset{-}{C}H_3}$ | 0.09 |
| −21.36 | 4*a* | $\pi_{\overset{+}{C}H_3}$ | 0.08 |
| −21.51 | 3*b* | $\pi_{\overset{-}{C}H_3}$ | 0.10 |

results of the CNDO/2 calculations are reported in table 3. On changing from He I to He II, bands A and C decrease in intensity relative to band B, and the components of band D also change in intensity. The variation of the calculated i.p. values with changing dihedral angle, $\phi$, is shown in fig. 3. The two highest occupied m.o.'s are mainly due to two sulphur non-bonding orbitals. The behaviour of the energy separation of these two orbitals for the various $\phi$ is similar to that of disulphides;[14] the separation is small at $\phi \sim 90°$, and large at $\phi = 0°$ and 180°. However, this splitting is the result of varying interactions of the S(3$p$) a.o.'s with the C$\equiv$C $\pi$-orbitals, rather than due to direct S—S interactions, as in the disulphides.

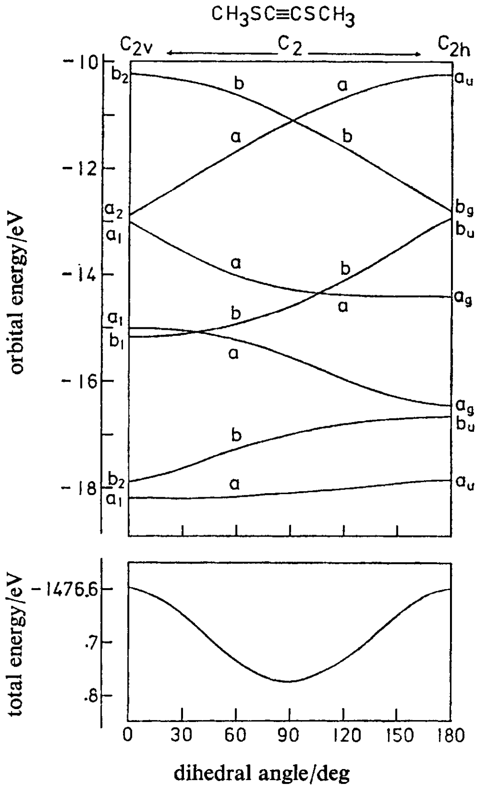

FIG. 3.—Variation of molecular orbital energy, calculated by CNDO/2 method, with dihedral angle $\phi$(CSSC) for $CH_3SC{\equiv}CSCH_3$.

There are generally two bands at low i.p. in the p.e. spectra of sulphides.[14-16] That at the lower i.p. is assigned to ionization from an out-of-plane, essentially S(3$p$) orbital, denoted $n_s$, and the other is assigned to an in-plane non-bonding orbital, $\sigma_s$. In disulphides, the combinations $n_s^+$, $n_s^-$ and $\sigma_s^+$, $\sigma_s^-$ are expected; the splitting of the $n_s$ pair is well documented, but splitting of the $\sigma_s$ pair is not always observed.[14-16] In acetylene, the $\pi_{C\equiv C}$ ionization occurs [17] at 11.40 eV. Bands corresponding to both of these constituents are expected in the low i.p. region of the p.e. spectrum of $(MeS)_2C_2$.

It has been observed that on changing from He I to He II excitation, ionization cross-sections of orbitals of second row elements decrease substantially when compared to corresponding cross-sections for first-row atoms. In a number of sulphur compounds it has been proposed that the intensity changes of p.e. bands can be accounted for mainly in terms of varying S(3*p*) population. On this basis it seems probable that the orbitals giving rise to bands A and C have much larger S(3*p*) character than those giving rise to band B. Since band C has a similar intensity to band A in both spectra, it is likely that there are two unresolved components. We assign band A to ionization of $n_s^+$ and $n_s^-$, band B to the acetylene $\pi$ orbitals, and band C to ionization of $\sigma_s^+$ and $\sigma_s^-$. The calculations agree with this assignment for band A, but appear to exaggerate the stabilization of the acetylene $\pi$ orbitals. It seems likely that the first component of band D also has some S(3*p*) character.

It is evident from the calculated behaviour of these orbitals as a function of torsion angle (fig. 3) that the possible structure mentioned in section 1 with no preferred torsional configuration can be ruled out. Such a structure would show three very broad bands at the position of bands A, B and C in fig. 2. Band A in particular would be expected to be at least 2 eV wide, and all three bands should have very similar double-humped envelopes. The observed spectrum is in good agreement with the calculation for a torsion angle close to 90°, except for the inversion of the $\sigma_s$ and $\pi_{C\equiv C}$ sets. The calculations of total energy also support a torsion angle close to 90° (see fig. 3).

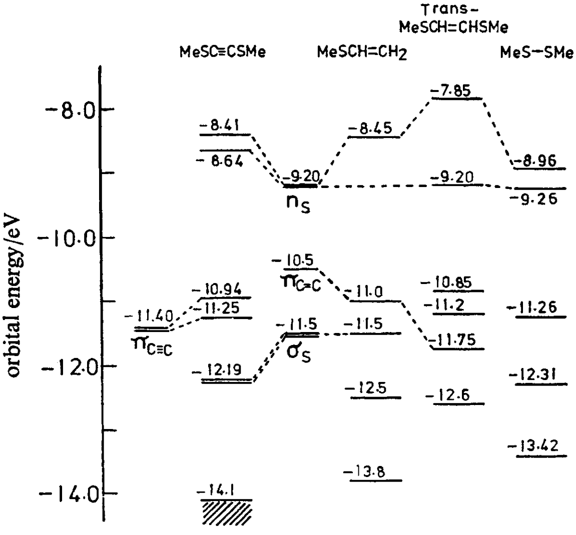

FIG. 4.—Molecular orbital correlation diagram for MeSC≡CSMe with MeSCH=CH$_2$ [ref. (14*a*)], *trans*-MeSCH=CHSMe [ref. (14*a*)] and Me$_2$S$_2$ [ref. (14*c*)].

In fig. 4 we attempt to correlate the spectrum with those of related compounds. We note that the splitting of $n_s^+$ and $n_s^-$ (band A) (0.23 eV) is similar to that in dimethyl disulphide (0.30 eV), but the much greater distance between the S atoms in 2,5-dithiahex-3-yne means that the splitting is more likely to be due to $n_s-\pi_{C\equiv C}$ interactions than $n_s-n_s$ through-space interaction. We have attempted to find appropriate values for the $n_s$ and $\sigma_s$ levels in the absence of any interactions of this type. Since $n_s^-$ in *trans*-CH$_3$SHC=CSHCH$_3$ cannot [14] interact with the $\pi$ level, the corresponding value of 9.20 eV seems appropriate; it is very similar to the value [14] 9.26 eV for $n_s^-$ in CH$_3$SSCH$_3$. Clearly there is a substantial destabilisation of both $n_s^+$ and $n_s^-$ from this value in (MeS)$_2$C$_2$, very similar to that of $n_s$ in CH$_3$SHC=CH$_2$ which arises from interaction with the $\pi$ orbital. In 2,5-dithiahex-3-yne both $n_s^+$ and $n_s^-$ can interact with the $\pi$ orbitals, and at a dihedral angle close to 90° the two interactions should be very similar. Estimation of a value for $\sigma_s$ in the absence of interaction is more difficult, but a value close to the $\pi_{C\equiv C}$ orbital of ethyne seems reasonable by comparison with the substituted ethenes. It is clear from fig. 3 that in $(MeS)_2C_2$ there is a stabilisation of $\sigma_s$ but a destabilisation of $\pi_{C\equiv C}$. In this molecule all three sets of orbitals, $n_s$, $\pi_{C\equiv C}$ and $\sigma_s$ have appreciable interactions with each other, and so there is evidence from the p.e. spectrum for electron delocalisation among these orbitals. However, these interactions are between sets of filled orbitals and any stabilisation of the molecule which might be inferred from the position of the $\sigma_s$ levels is counteracted by the destabilisation of $n_s^+$, $n_s^-$ ; no net C—S bonding can be deduced from the p.e. spectrum, though a small stabilisation could not be ruled out.

## VIBRATIONAL SPECTRA OF 2,5-DITHIAHEX-3-YNE

The results of the preceding sections have shown clearly that in the vapour phase 2,5-dithiahex-3-yne adopts a conformation which is neither purely *cis* ($\phi = 0°$ ; $C_{2v}$) nor purely trans ($\phi = 180°$ : $C_{2h}$). We were not able to record the Raman spectrum in the gas phase, but Raman and infrared spectra of the pure liquid $(MeS)_2C_2$ were obtained and show a number of interesting features (table 4). If the heavy atom skeleton [CSCCSC] is considered in isolation, then 12 fundamental vibrations are expected. In the centrosymmetric *trans* conformation, mutual exclusion would operate between infrared and Raman active modes [5 stretching vibrations, $3A_g$(Raman) ; $2B_u$(i.r.). 7 bending vibrations, $2A_g+B_g$(Raman) ; $2A_u+2B_u$(i.r.)], whereas this exclusion would not operate in the *cis* conformation.

TABLE 4.—INFRARED AND RAMAN SPECTRA OF $CH_3SC\equiv CSCH_3$

| $\nu$/cm$^{-1}$ (i.-r.) | $\nu$/cm$^{-1}$ (Raman) | possible assignment |
|---|---|---|
| 3001 (33)[a] | 3001 dp[b] (8)[a] | $\nu_{as}$(C—H)$CH_3$ |
| 2921 (98) | 2926 p (71) | $\nu_s$(C—H)$CH_3$ |
| 2830 (6) | 2823 p (3) | |
| 2812 (8) | | |
| 2603 (2) | 2609 p (0.5) | |
| | 2557 p (1) | |
| | 2082 p (100) | $\nu(C\equiv C)$ |
| 2073 (5) | | |
| | 1874 p (2) | |
| 1433 (77) | | |
| 1422 (70) | 1422 dp (2) | $\delta_{as}(CH_3)$ |
| 1312 (100) | 1314 p (8) | $\delta_s(CH_3)$ |
| 976 (85) | 975 dp (1) | $\delta(CH_3)\perp$ |
| 958 (51) | | $\delta(CH_3)\|\|$ |
| 942 (33) | 946 dp (0.5) | |
| | 683 p (44) | $\nu_s$(C—S) |
| | 476 p (3) | $\delta(SCC)\|\|$ |
| 415 (5) | | |
| | 392 p (1) | $\delta(SCC)\perp$ |
| 290 (10) | 290 p (5) | $\delta(CSC)\|\|$ |

[a] Intensity (peak height) relative to that of the most intense peak in the spectrum. [b] p = polarised, dp = depolarised. Bands are considered polarised if $I_{\|}/I_{\perp} > 1.8$ where $I$ is the full width at half maximum.

The rigour of the selection rules can be expected to break down in the liquid-phase spectra because of intermolecular interactions, and the observed spectra show that mutual exclusion is not complete. Several Raman active bands (at 392, 476, 683, 946 and 2082 $cm^{-1}$) are either absent or very weak in the i.r. spectrum, and some i.r. active bands (at 412, 938, 955 $cm^{-1}$) are absent from the Raman spectrum. These observations suggest that in the liquid state 2,5-dithiahex-3-yne adopts a conformation which, while neither *cis* nor *trans*, is probably nearer the latter.

The vibrations of the $CH_3$ groups may be assigned by reference to the infrared and Raman spectra of MeSCN [18] and MeSC≡CH.[19] The symmetric stretch, $\nu(C{\equiv}C)$ can then be assigned to the intense polarised band at 2082 $cm^{-1}$ in the Raman spectrum, which is absent from the infrared spectrum. This frequency is to be compared with that [20] in $(CF_3S)_2C_2$ (2110 $cm^{-1}$) and that [21] in but-2-yne (2238 $cm^{-1}$).

The other vibrations of the $(C_4S_2)$ skeleton are expected to occur in the region below 800 $cm^{-1}$. On the basis of comparison with the spectra of MeSCN [18] and MeSC≡CH,[19] we assign the strong polarised Raman band at 683 $cm^{-1}$ to the symmetric $\nu(C{-}S)$ vibration, and the weaker polarised bands at 476 and 392 $cm^{-1}$ to SCC bending vibrations parallel and perpendicular to the molecular plane respectively. These bands are absent from the infrared spectrum. The lowest frequency (>50 $cm^{-1}$) vibration at 290 $cm^{-1}$ is assigned to bending at sulphur ($\widehat{CSC}$) parallel to the molecular plane. There is a broad, low intensity band centred at this frequency in the infrared spectrum.

### N.M.R. SPECTRA

A singlet in the $^1H$ n.m.r. spectrum ($\delta$ = 2.40 p.p.m.) of $(MeS)_2C_2$ shows a slight shift to lower field from the position of the corresponding signal in $Me_2S$ ($\delta$ = 2.02 p.p.m.) [22] and in $MeSCH{=}CH_2$ ($\delta$ = 2.12 p.p.m.).[23] The $^{13}C$ n.m.r. spectrum shows a quartet centred at $\delta$ = 19.0 p.p.m. ($^1J$ = 135 Hz) produced by the methyl carbons, and a quartet centred at $\delta$ = 88.5 p.p.m. ($^3J$ = 58 Hz) produced by the acetylenic carbon atoms. The shift of the *sp*- carbon atoms differs very little from that [24] in hex-3-yne ($\delta$ = 82.2 p.p.m.), indicating that substitution of a methylene group by a sulphur(II) atom does not cause a net shift of charge between the sulphur atoms and the triple bond in a symmetrical acetylene.[24]

### U.V./VISIBLE SPECTRUM

A single band ($\lambda_{max}$ 246 nm, log $\varepsilon$ 2.36) in the u.v./visible spectrum of $(MeS)_2C_2$ is attributable to the $\pi$-$\pi^*$ transition of the (C≡C) bond. The bathochromic shift of ~20 nm from hex-3-yne ($\lambda_{max}$ 223 nm, log $\varepsilon$ 2.29), is similar to that observed [20] in $(CF_3S)_2C_2$ ($\lambda_{max}$ 250 nm, log $\varepsilon$ 2.42).

## CONCLUSION

The question of conjugation in acetylenic ethers and thioethers has been in dispute for some years, with particular reference to ethynyl compounds. Measurement of the dipole moments [25] of RXC≡CH (X = O, S) and the ethynyl proton chemical shift [26] of the same compounds, led to the view that resonance effects involving contributions from structures containing multiple bonds between sulphur and carbon such as

$$R\overset{+}{S}{=}C{=}\overset{-}{C}{-} \leftrightarrow R\overset{-}{S}{=}C{=}\overset{+}{C}{-}$$

were important, and this was supported by the observed reactivity of alkynyl thioethers towards nucleophiles.[27] It has been suggested [19] that the decrease in $\nu(C{\equiv}C)$ from its value in propyne (2142 $cm^{-1}$) to that in MeSC≡CH (2059 $cm^{-1}$) is explicable in terms of conjugation between sulphur and the C≡C link.

A reassessment [24] of the n.m.r. evidence suggested the effects of conjugation or resonance must be very small. Structural studies showed [7, 28] no evidence for conjugation in the S—C($sp$) bond on the basis of the length of that bond in RS—C≡CH, but the observed interdependence of $\widehat{CSC}$ bond angle and S—C($sp^3$) bond length made this conclusion ambiguous.

The results we have described, which are the first relating to an acetylenic dithioether, show that there is no definite evidence of a $\pi$-type interaction between the sulphur atoms and the triple bond. In particular, the stabilisation of $\sigma_s$ as a result of interaction with $\pi_{C\equiv C}$ is exactly counter-balanced by the destabilisation of $n_s$ as a result of interaction with the same system.

We thank the S.R.C. for support, and Dr. I. W. Parsons for the use of his CNDO/2 program.

[1] J. A. Connor and G. A. Hudson, *J. Organometallic Chem.*, 1975, **97**, C43; G. A. Hudson, *Ph.D. Thesis* (Manchester University, 1975).

[2] N. J. Taylor, H. N. Paik, P. C. Chieh and A. J. Carty, *J. Organometallic Chem.*, 1975, **87**, C31.

[3] A. G. Robiette, *Molecular Structure by Diffraction Methods*, 1973, **1**, 160.

[4] M. Tanimoto, K. Kuchitsu and Y. Morino, *Bull. Chem. Soc. Japan*, 1969, **42**, 2519.

[5] B. Beagley and K. T. McAloon, *Trans. Faraday Soc.*, 1971, **67**, 3216.

[6] S. Samdal and H. M. Seip, *Acta Chem. Scand.*, 1971, **25**, 1903; S. Samdal and H. M. Seip, *J. Mol. Struct.*, 1975, **28**, 193.

[7] D. den Engelsen, *J. Mol. Spectr.*, 1969, **30**, 474.

[8] H. Dreizler, H. D. Rudolph and H. Schleser, *Z. Naturforsch.*, 1970, **25A**, 1643.

[9] T. Fukuyama, K. Kuchitsu, Y. Tamaru, Z. Yoshida and I. Tabushi, *J. Amer. Chem. Soc.*, 1971, **93**, 2799; K. Karakida and K. Kuchitsu, *Bull. Chem. Soc. Japan*, 1975, **48**, 1691; Z. Nahlovska, B. Nahlovsky and H. M. Seip, *Acta Chem. Scand.*, 1969, **23**, 3534.

[10] M. Tanimoto, K. Kuchitsu and Y. Morino, *Bull. Chem. Soc. Japan*, 1969, **42**, 2519.

[11] L. S. Bartell and H. K. Higginbotham, *J. Chem. Phys.*, 1965, **42**, 851.

[12] D. P. Santry and G. A. Segal, *J. Chem. Phys.*, 1967, **47**, 158; J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory* (McGraw-Hill, New York, 1970).

[13] A. Katrib, T. P. Debies, R. J. Colton, T. H. Lee and J. W. Rabalais, *Chem. Phys. Letters*, 1973, **22**, 196; A. Schweig and W. Thiel, *Mol. Phys.*, 1974, **27**, 265.

[14] (*a*) H. Bock, G. Wagner, K. Wittel, J. Sauer and D. Seebach, *Chem. Ber.*, 1974, **107**, 1869; (*b*) A. D. Baker, M. Brisk and M. Gellender, *J. Electron Spectr.*, 1974, **3**, 227; (*c*) K. Kimura and K. Osafune, *Bull. Chem. Soc. Japan*, 1975, **48**, 2421.

[15] H. Bock and G. Wagner, *Angew. Chem.*, 1972, **84**, 119; G. Wagner and H. Bock, *Chem. Ber.*, 1974, **107**, 68.

[16] R. J. Colton and J. W. Rabalais, *J. Electron Spectr.*, 1974, **3**, 345; W. Schäfer and A. Schweig, *Z. Naturforsch.*, 1975, **30A**, 1785.

[17] D. W. Turner, C. Baker and C. R. Brundle, *Molecular Photoelectron Spectroscopy* (Wiley-Interscience, London, 1970).

[18] A. G. Moritz, *Spectrochim. Acta*, 1966, **22A**, 1021.

[19] A. G. Moritz, *Spectrochim. Acta*, 1967, **23A**, 167.

[20] J. F. Harris, *J. Org. Chem.*, 1967, **32**, 2063.

[21] B. L. Crawford, *J. Chem. Phys.*, 1939, **7**, 555.

[22] J. T. Wang and C. H. Van Dyke, *Inorg. Chem.*, 1968, **7**, 1319.

[23] M. C. Caserio, R. E. Pratt, and R. J. Holland, *J. Amer. Chem. Soc.*, 1966, **88**, 5747.

[24] D. Rosenberg and W. Drenth, *Tetrahedron*, 1971, **27**, 3893; D. Rosenberg, J. W. BeHaan and W. Drenth, *Rec. Trav. Chim.*, 1968, **87**, 1387.

[25] W. Drenth, L. Hekkert and B. G. Zwanenberg, *Rec. Trav. Chim.*, 1962, **81**, 313.

[26] W. Drenth and W. Lowenstein, *Rec. Trav. Chim.*, 1962, **81**, 635.

[27] H. C. Volger and J. F. Arens, *Rec. Trav. Chim.*, 1958, **77**, 1170.

[28] A. Bjorseth, *J. Mol. Struct.*, 1974, **23**, 1.

[29] L. Brandsma, *Preparative Acetylene Chemistry* (Elsevier, Amsterdam, 1971), p. 194.

[30] B. Beagley, A. H. Clark and T. G. Hewitt, *J. Chem. Soc. A*, 1968, 658; W. Zeil, J. Haase and L. Wegmann, *Z. Instrumenttech.*, 1966, **74**, 84.

[31] B. Beagley, J. J. Monaghan and T. G. Hewitt, *J. Mol. Struct.*, 1971, **8**, 401.

[32] D. R. Lloyd, *J. Phys. E*, 1970, **3**, 629.

(PAPER 6/2238)