X-Ray, N.M.R., and Theoretical Studies of the Structures of (Ethylthio)bullvalene

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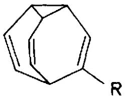
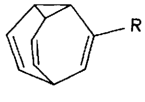
The structure of (ethylthio)bullvalene has been determined in solution and solid state. Whereas the structure of the title compound in the crystal is 4-(ethylthio)tricyclo[3.3.2.$0^{2,8}$]deca-3,6,9-triene, in solution a mixture of the 4-(ethylthio)- (15%) and 3-(ethylthio)-bullvalene (85%) has been detected. The dynamics of the valence tautomerism has been studied by variable temperature ^{1}H n.m.r. spectroscopy. A comparison between the experimentally determined thermodynamic and kinetic quantitites of the valence tautomerism with MINDO/3, MNDO, and force-field calculations shows very good agreement between theory and experiment.

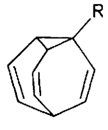
The prediction of the remarkable dynamic structure of bullvalene by Doering and Roth[1] in 1962 and the synthesis of the compound by Schröder[2] with experimental verification of its fast valence tautomerism are milestones in modern organic chemistry. The dynamic structure of bullvalene has been extensively studied in solution and the solid state.[3] The goal of our study was to investigate the structure and dynamics of a simple monosubstituted derivative, (ethylthio)bullvalene.



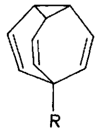
O_B



O_C



C



B

R = SCH_2CH_3

Central to our study is the question which of the four different valence tautomers (O_B, O_C, C, and B) are present in solution and in the solid state? In addition, it was thought that a comparison between theoretical calculations and temperature-dependent n.m.r. experiments should result in at least qualitative information about the kinetic and thermodynamic stabilities of the valence tautomers.

Results and Discussion

Crystal Structure.—The molecular structure of (ethylthio)bullvalene in the crystalline state is shown in Figure 1. The atom numbering scheme and relevant bond lengths are given in Figure 2. The ethylthio group is substituted on C(4) of the bullvalene skeleton, hence the O_B valence tautomer is present in the solid state. The sulphur atom S(11) and carbon C(12) are coplanar with the C(3)–C(4) double bond as indicated by the torsion angle C(12)–S(11)–C(4)–C(3) = 1.0(5)°. The terminal methyl carbon atom is out-of-plane, the torsion angle C(13)–C(12)–S(11)–C(4) being 79.4(4)°.

A detailed analysis of all bond lengths and angles (Figure 2, Table 2) indicates a small but significant deviation of the bullvalene geometry from the expected threefold symmetry. The deviation is especially striking in the cyclopropane ring, the C–C bond C(1)–C(8) being unusually long (156.4 pm) and thus about 4 pm longer than the other two bonds, C(1)–C(2) (152.8 pm) and C(2)–C(8) (151.8 pm), in the ring. This asymmetry also causes a deviation of the C–C–C bond angles in the cyclopropane ring from their ideal value of 60°. The angles at C(1) [58.6(3)°] and C(8) [59.5(3)°] are smaller and the angle at C(2) [61.9(3)°] is significantly larger than normal.

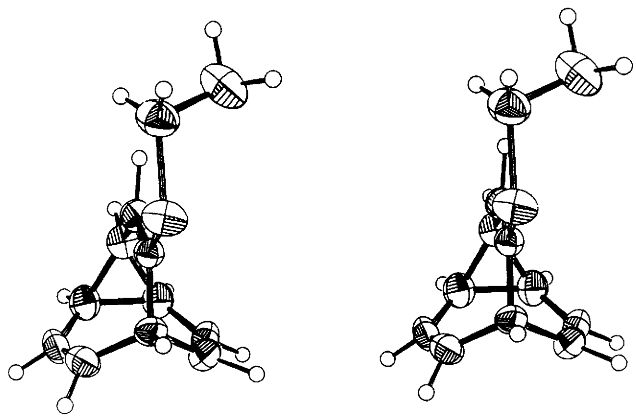
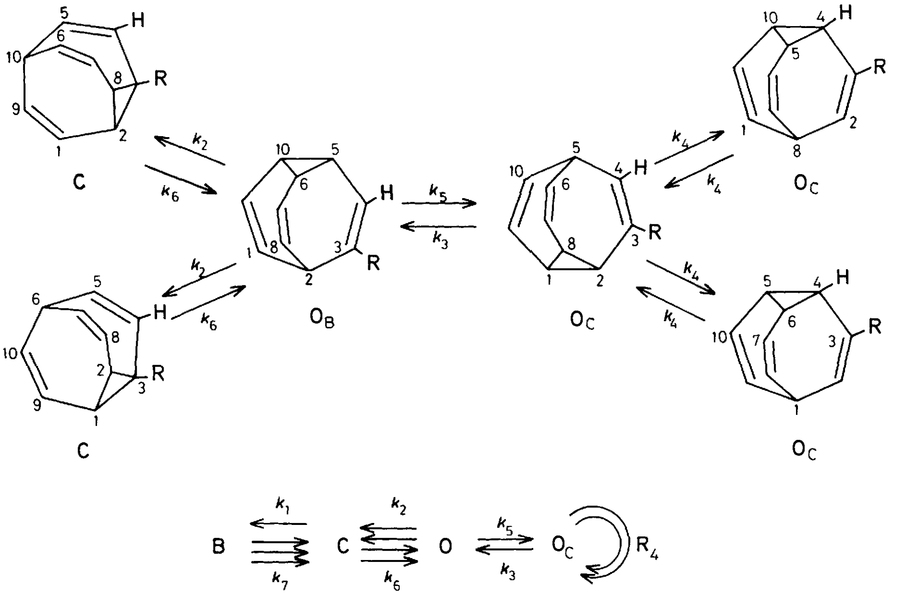


Figure 1. Molecular structure of (ethylthio)bullvalene as derived from *X*-ray analysis.[8]

Further discrepancies are observed for the three C(sp^2)–C(cyclopropane) bond lengths. C(2)–C(3) (148.5 pm) is longer than C(1)–C(9) (145.8 pm) and C(8)–C(7) (145.2 pm). Moreover, the valence angle C(10)–C(5)–C(6) is smaller by more than 3° than the two other C–C–C bond angles at C(5). Thus, the intramolecular contact C(10)–C(6) is shortened to 244.7 pm, whereas C(4)–C(10) and C(6)–C(4) are 249.4 and 250.6 pm. Considering the values of all the bond lengths and angles, the structure of the bullvalene skeleton in (ethylthio)bullvalene can better be described by mirror rather than threefold symmetry.

The same tendency concerning molecular symmetry was found in the room-temperature *X*-ray analysis of bullvalene itself[3] and interpreted by the authors in terms of crystal-packing effects. In a recent[4] neutron-diffraction study of bullvalene at 110 K we have shown that crystal packing influences are rather weak, leading only to marginal deviations from the ideal threefold symmetry.

The present asymmetries in the molecular structure of (ethylthio)bullvalene may be caused by the π-donor properties of the ethylthio group. Allen[5] has shown that substituents of this type cause a lengthening of the opposite endocyclic C–C bond in monosubstituted cyclopropane derivatives by 2.5–6 pm, which is in agreement with the value of C(1)–C(8) = 156.4 pm (lengthening of 4 pm) found in (ethylthio)bullvalene. From a



Scheme.

Table 1. Atomic parameters of (ethylthio)bullvalene, U_{eq} values in 100 A^2.

Atom	x	y	z	U_{eq}
C(1)	0.361 6(2)	0.361 5(2)	0.350 3(9)	4.7(5)
C(2)	0.275 3(2)	0.361 6(2)	0.377 3(9)	4.3(4)
C(3)	0.229 7(2)	0.432 6(2)	0.376 7(9)	4.1(4)
C(4)	0.241 3(1)	0.491 7(1)	0.256 4(9)	3.6(3)
C(5)	0.304 5(2)	0.496 1(2)	0.097 4(8)	4.0(4)
C(6)	0.297 7(2)	0.433 9(2)	−0.063 4(9)	4.7(4)
C(7)	0.299 3(2)	0.360 5(2)	−0.020(1)	4.7(4)
C(8)	0.307 8(2)	0.326 2(2)	0.183(1)	5.1(5)
C(9)	0.404 6(2)	0.430 6(2)	0.307 7(9)	4.6(5)
C(10)	0.381 5(1)	0.489 0(3)	0.199 1(9)	4.6(5)
S(11)	0.184 85(5)	0.575 01(4)	0.253 4(2)	5.1(2)
C(12)	0.112 1(2)	0.559 8(3)	0.450(1)	5.6(5)
C(13)	0.139 0(3)	0.573 4(3)	0.667(1)	7.1(6)
H(1)	0.391(2)	0.318(2)	0.43(1)	6(1)
H(2)	0.259(2)	0.330(2)	0.474(8)	2.7(9)
H(3)	0.193(2)	0.432(2)	0.480(9)	3.6(9)
H(5)	0.298(2)	0.549(2)	0.03(1)	5(1)
H(6)	0.301(3)	0.454(3)	−0.22(2)	10(2)
H(7)	0.293(3)	0.333(3)	−0.12(1)	7(2)
H(8)	0.304(3)	0.265(3)	0.19(1)	10(2)
H(9)	0.460(3)	0.424(2)	0.36(1)	7(1)
H(10)	0.413(3)	0.536(3)	0.19(1)	7(1)
H(121)	0.085(2)	0.513(3)	0.44(1)	7(1)
H(122)	0.076(2)	0.596(2)	0.43(1)	6(1)
H(131)	0.170(3)	0.523(4)	0.72(2)	13(2)
H(132)	0.085(3)	0.559(3)	0.79(1)	8(2)
H(133)	0.151(3)	0.631(3)	0.67(1)	9(2)

systematic analysis of diffraction data for vinyl substituted cyclopropane derivatives, Allen[5] has calculated averages for the C–C (ring), the C(ring)–C(sp^2) and the C=C bond lengths, which are 152.0, 146.5, and 133.6, respectively. The present data for (ethylthio)bullvalene are in rough agreement with these values (153.5, 146.5, and 131.5 pm), but the C=C bond is somewhat shorter than expected.

Structure in Solution.—The ^{1}H n.m.r. spectra of (ethylthio)bullvalene in deuteriated dichloromethane and dimethyl sulphoxide are given in Figure 3.

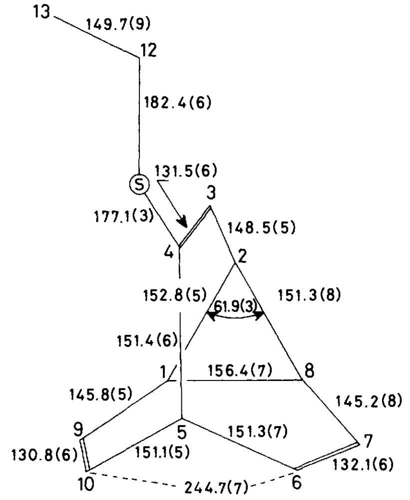


Figure 2. Atom numbering scheme and bond lengths in pm (e.s.d.s in parentheses).

Table 2. Bond angles in (ethylthio)bullvalene in degrees (e.s.d.s in parentheses).

Bonds	Angle/°	Bonds	Angle/°
C(2)–C(1)–C(8)	58.6(3)	C(4)–C(5)–C(10)	111.1(4)
C(2)–C(1)–C(9)	122.4(3)	C(6)–C(5)–C(10)	108.0(3)
C(8)–C(1)–C(9)	121.0(5)	C(5)–C(6)–C(7)	124.1(5)
C(1)–C(2)–C(3)	122.5(3)	C(6)–C(7)–C(8)	126.8(5)
C(1)–C(2)–C(8)	61.9(3)	C(1)–C(8)–C(2)	59.5(3)
C(3)–C(2)–C(8)	123.3(5)	C(1)–C(8)–C(7)	121.4(3)
C(2)–C(3)–C(4)	125.7(4)	C(2)–C(8)–C(7)	122.6(3)
C(3)–C(4)–C(5)	123.7(3)	C(1)–C(9)–C(10)	126.5(3)
C(3)–C(4)–S(11)	125.0(3)	C(5)–C(10)–C(9)	125.1(3)
C(5)–C(4)–S(11)	111.3(3)	C(4)–S(11)–C(12)	105.3(2)
C(4)–C(5)–C(6)	111.8(3)	S(11)–C(12)–C(13)	114.1(3)

The room-temperature spectrum shows sharp signals for the ethylthio group but only two very broad signals in the aliphatic and alkene region. Below −40 °C, all signals in the spectrum are sharp. The intensity ratio between alkene and aliphatic proton integrals is 5:4, showing unambiguously the substitution of an

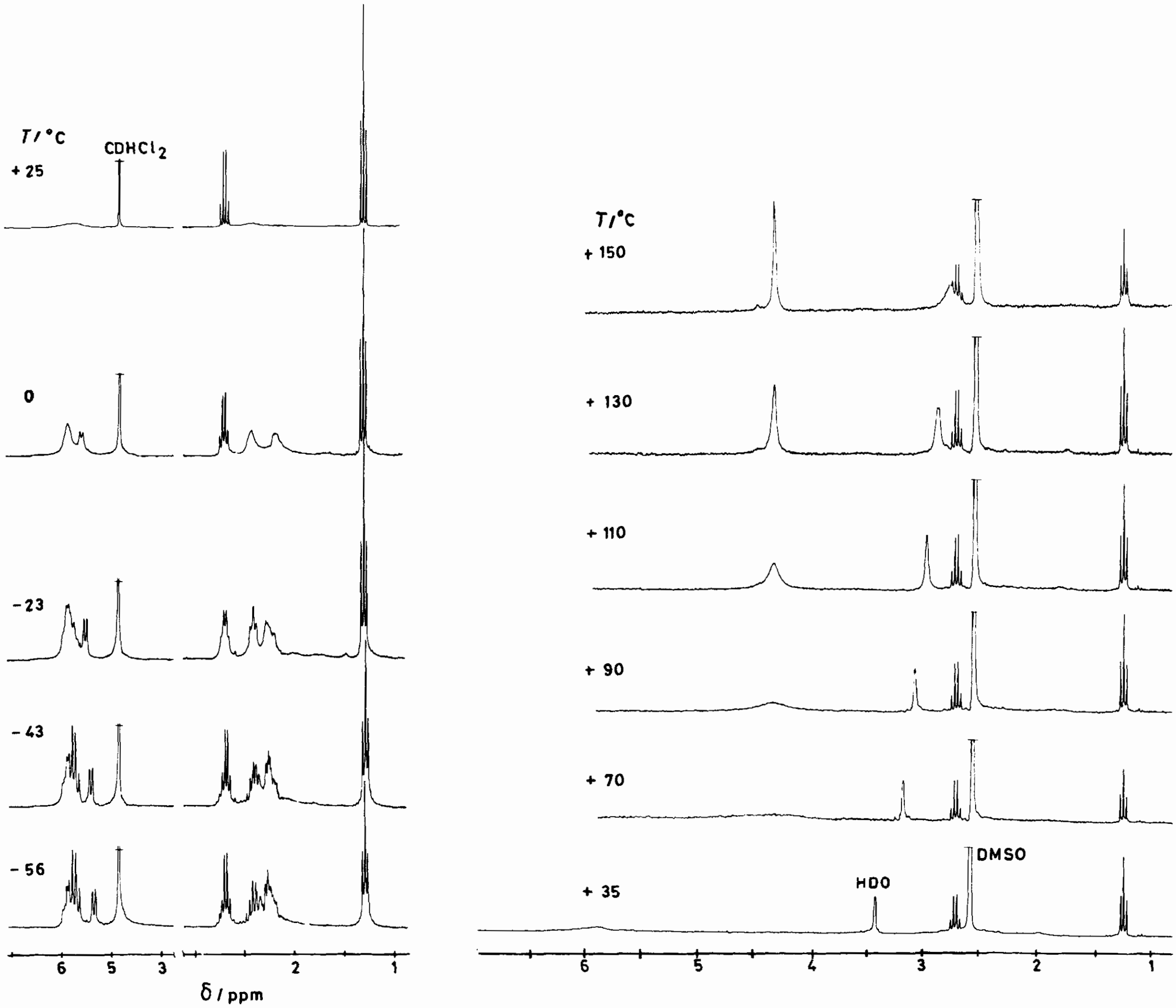


Figure 3. ^{1}H N.m.r. spectrum of (ethylthio)bullvalene at different temperatures. Residual proton signals arising from the perdeuteriated dichloromethane and dimethyl sulphoxide are indicated.

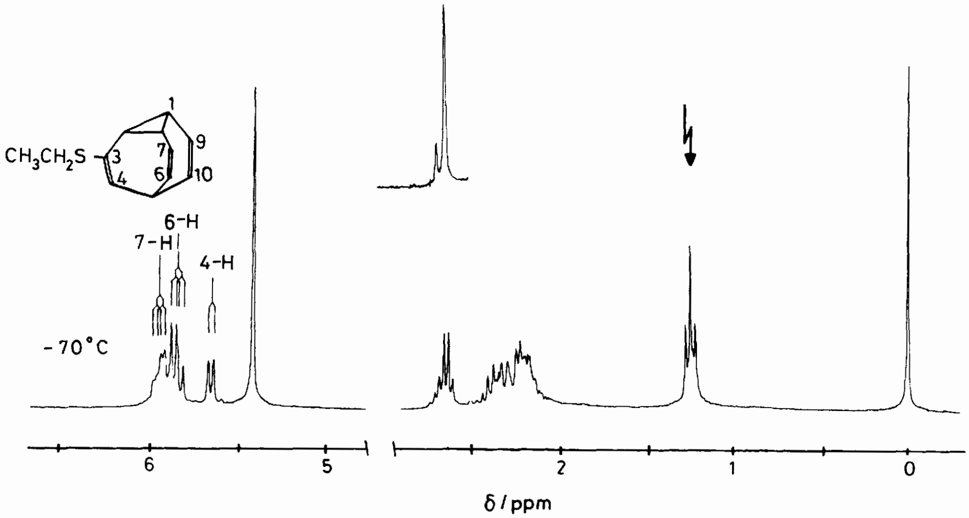


Figure 4. Low-temperature ^{1}H n.m.r. spectra of (ethylthio)bullvalene with and without irradiation of a double resonance r.f. field into the spectral region of the methyl groups.

alkenic proton by the ethylthio group. In a double resonance experiment, irradiation of the methyl group at δ 1.25 simplifies the signals of the CH_2 protons to two singlets with a relative intensity ratio of 85:15 at −56 °C. Thus, in solution, a mixture of 3- and 4-(ethylthio)bullvalene is present (Figure 4).

In order to determine which of the two valence tautomers is

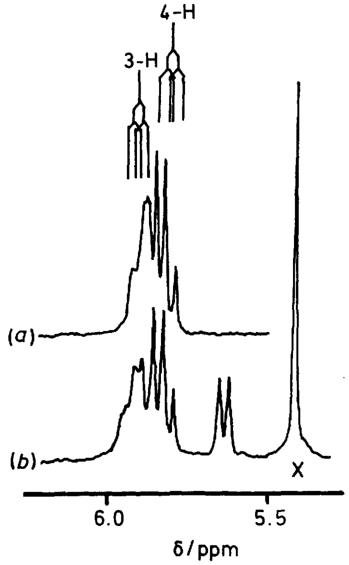


Figure 5. Comparison between the low-temperature (−70 °C) ^{1}H n.m.r. spectra of bullvalene (*a*) and (ethylthio)bullvalene (*b*) in deuteriated dichloromethane (X = residual solvent signal).

in higher concentration and therefore thermodynamically more stable, we measured unsubstituted bullvalene for comparison (Figure 5).

Application of double-resonance techniques showed that the proton signal in bullvalene at lowest field corresponds to 3-H, which is coupled to 4-H ($J_{3,4}$ 11.1 Hz) and shows a vicinal coupling to 2-H and several long-range couplings to the cyclopropane protons.[6] The signal due to 4-H is observed as a sharp doublet of doublets ($J_{3,4}$ 11.1 and $J_{4,5}$ 8.3 Hz). The comparison between the bullvalene and its monosubstituted derivative shows clearly that the high-field doublet at δ 5.70 in (ethylthio)bullvalene is not broadened due to long-range couplings and thus corresponds to the 4-H of the 3-ethylthio isomer. Therefore the structure of the main isomer corresponds to the O_C valence tautomer and the minor isomer is the O_B valence tautomer (see the Scheme).* The energy difference between the two isomers can be calculated from the concentration ratio and is 3.1 kJ mol^{-1} at −56 °C.

The temperature-dependent spectra of all exchanging 10-spin systems of all four valence tautomers with their unknown concentrations and chemical shifts cannot be analysed quantitatively. Only qualitative information can be obtained with respect to the thermodynamic stabilities and the rate of valence tautomerisation. At high temperatures only one sharp singlet is observed, showing that, in fast exchange, each proton goes through all different molecule positions. This is only possible when the total rearrangement cycle contains the O_C, O_B, and C isomers. There is no direct experimental evidence for the presence or absence of the valence tautomer B in the equilibrium.

Furthermore, the time-dependent spectra show that the doublet due to 4-H broadens at relatively high temperatures compared with the other signals. At 0 °C the coupling of 11.1 Hz can be easily detected while all other signals show half widths of *ca.* 30–35 Hz. This smaller line width of the alkenic 4-H demonstrates that those isomerizations are preferred in which this proton does not change its chemical shift drastically retaining its alkene character. Therefore k_4 must be smaller than k_3, and the activation energy of the isomerization of the thermodynamically most stable O_C isomer into an identical O_C isomer is larger than the isomerization into the less stable O_B valence tautomer. In addition, using of the experimentally determined value of 5.7 for the equilibrium constant $K = k_5/k_3$, the order of isomerization rates is found to be $k_5 > k_3 > k_4$.

Empirical and Semiempirical Calculations.—In addition to the experimental investigations, molecular-mechanics calculations using the force field implemented in CHEMGRAPH[9] and semiempirical MINDO/3[10] and MNDO[11] calculations were executed. Initially, the room-temperature *X*-ray data of bullvalene and the O_B-isomer structure of (ethylthio)bullvalene were used as input data for a complete geometry optimization with MINDO/3 and MNDO. No symmetry constraints were introduced. Nevertheless all calculations converged towards the bullvalene molecular structure with almost perfect threefold symmetry, although a non-symmetric model was input. The results of these optimizations given in Table 3 show a rather close correspondence between experimental (*X*-ray and neutron diffraction) and theoretical data.

In order to determine the relative thermodynamic stabilities of the different valence tautomers of (ethylthio)bullvalene and to obtain information about the preferred conformation of each isomer, force-field (CHEMGRAPH) and MINDO/3 calculations were performed as follows: for each of the four isomers, a complete two-dimensional molecular-mechanics calculation was performed with respect to the conformation of the ethylthio group. The conformation was systematically varied in terms of the two torsion angles σ [along the C(ethyl)–S–bond] and τ [along the S–C(bullvalene) bond]. The results of the empirical CHEMGRAPH calculations displayed as two-dimensional Ramachandran plots show minor variations along σ but sharp minima in τ-direction, especially at τ = ±90° (Figure 6).

In view of these results and to save computer time, only τ was varied systematically as the reaction co-ordinate in the corresponding MINDO/3 calculations, and σ was optimized for each τ value, resulting generally in σ-values close to 180°. The results of the MINDO/3 calculations are in close agreement with the force-field calculations [see Figure 6(*b*)]. Moreover, they allow an estimate of the energy differences between the different isomers. As Table 4 shows O_C is more stable than O_B by 2.1 kJ mol^{-1}, whereas the B and C isomers are considerably less favoured. These findings confirm the n.m.r. results from which the O_B isomer was found to be 3.1 kJ mol^{-1} higher in energy than the O_C isomer at −56 °C.

It should be pointed out that in the O_C and O_B valence tautomers the theoretically favoured conformation of the ethylthio group was found at 90°. However, in the crystal structure τ was close to 0 °C for the O_B isomer.

The consistency between empirical and semiempirical calculations on the one hand and the agreement between theoretical data and n.m.r. experiments on the other hand, encouraged us to extend our calculations to the transition state. First the bullvalene transition-state geometry was generated with MINDO/3 by a systematic opening of one cyclopropane bond, assuming an *mm*2 symmetry of the transition state (Figure 7).

With the transition-state geometry of the bullvalene skeleton fixed, the energies of the various transition states for all four valence tautomers of (ethylthio)bullvalene were then determined.

Assuming an *mm*2 symmetry in the transition state, the ethylthio group can have the four positions O (substituted to the isolated double bond), B_M (substituted to a mirror symmetric position at the opened three membered ring), A and A_M (substituted to the delocalized double bond, A_M a mirror

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* Based on 50 MHz low-temperature n.m.r. spectra Oth *et al.*[7] could detect only one isomer in various (alkylthio)bullvalenes. Owing to the low spectral resolution of the n.m.r. spectrometers at that time, the structure assignment (O_B) is based only on statistical arguments.

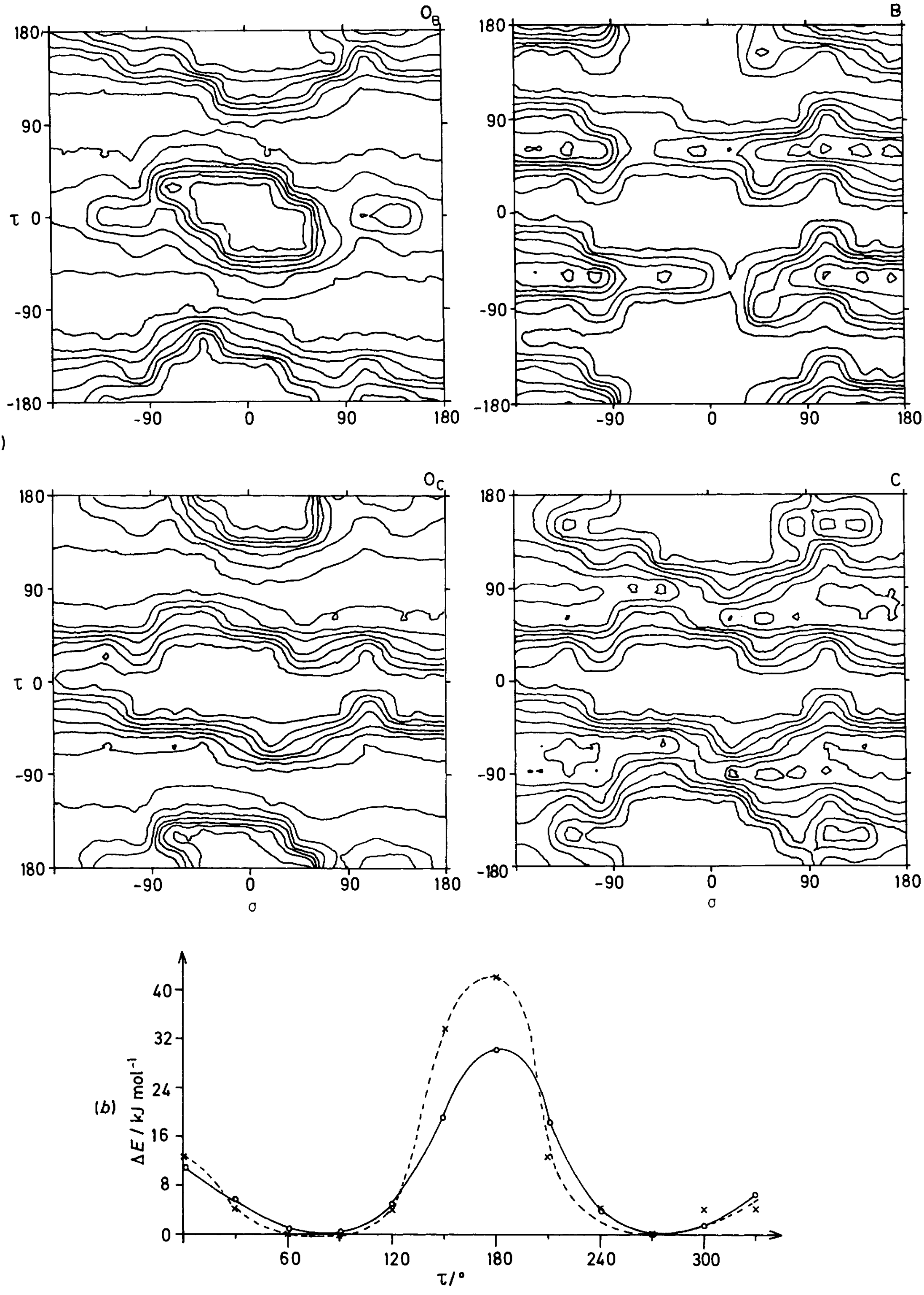
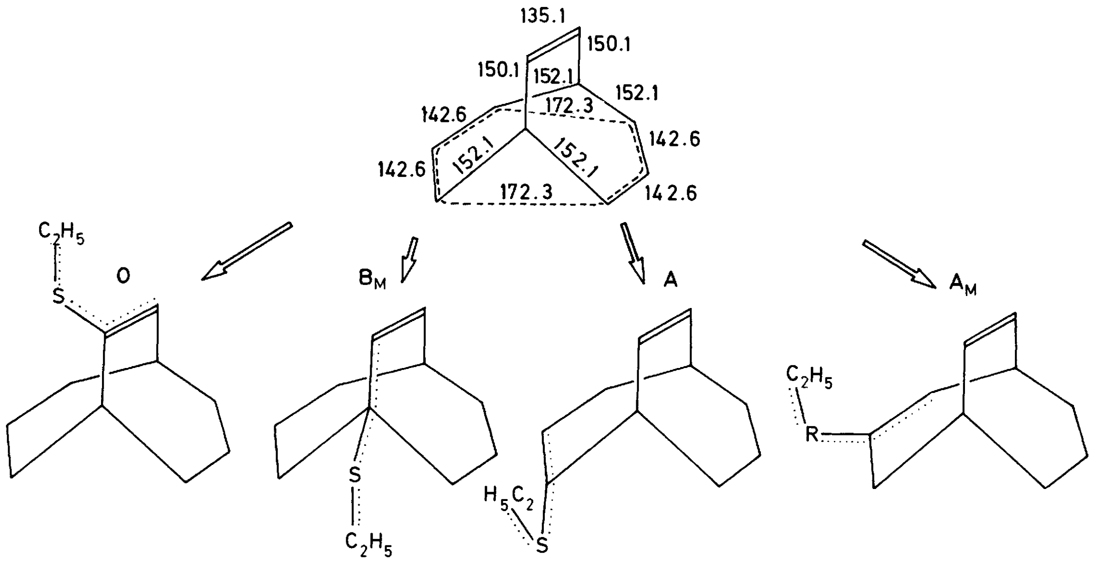


Figure 6. Two-dimensional conformation-energy distribution in terms of the torsion angles σ and τ of the ethylthio group, generated with the CHEMGRAPH force field for all four isomers O_B, B, O_c, and C (*a*). Results of (one-dimensional) MINDO/3 (——) and force-field (- - - -) calculations in terms of τ for the O_B isomer (*b*).

symmetric position, see Figure 7). For all four isomers O, B_M, A, and A_M similar MINDO/3 calculations as for the ground state were executed, *i.e.* the torsion angle τ was systematically varied and σ was optimized for each τ (generally to values close to 180°). The results are shown in Figure 7.

Summarizing the results of the MINDO/3 calculations for the ground and transition state, the reaction profiles displayed in Figure 8 can be generated. The theoretical calculations totally validate the relative concentrations of the different isomers ($O_C > O_B \gg$ B, C) and agree also with the order of rearrangement rates $k_5 > k_3 > k_4$ extracted from the n.m.r. measurements. The unexpected experimental finding that the



Isomer	ΔE/kJ mol^{-1}	τ/°
O	0	0
B_M	17.6	180
A	10.5	30
A_M	5.0	0

Figure 7. MINDO/3-based relative energies of all transition states within the rearrangement between the (ethylthio)bullvalene isomers assuming the geometry of the transition state of bullvalene. The definition of the torsion angle τ can be obtained from the dashed bonding sequence.

Table 3. Survey of some averaged bond lengths (in pm) in the bullvalene skeleton. Each value corresponds to the average over the three chemically equivalent bonds. The numbers enclosed in parentheses indicate the maximum deviation from the averaged value, and thus constitute a measure of the asymmetry within the molecule.

Bond	C–C(cyclopr.)	C(cyclopr.)–C(sp^2)	C(sp^2)–C(sp^2)	C(sp^2)–C(sp^3)	C–H
(*a*) Bullvalene					
X-Ray (295 K)	153.9(36)	145.2(12)	131.9(11)	150.9(9)	108(25)
X-Ray (110 K)	153.4(6)	147.1(1)	133.6(2)	151.6(4)	96(3)
Neutron (110 K)	153.30(47)	147.26(26)	134.23(14)	151.65(7)	108.9(9)
Neutron[b]	153.96(50)	147.88(25)	134.79(14)	152.30(2)	109.4(9)
MINDO/3	154.1	149.3	135.3	152.6	109(–)[a]
MNDO	155.2	148.5	135.1	152.2	109(–)[a]
(Theor.-X)	0.8	3.7	3.3	1.5	—
(Theor.-N_{Th})	0.7	1.0	0.4	0.1	—
(*b*) Ethylthiobullvalene					
X-Ray (295 K)	153.5(51)	146.5(33)	131.5(13)	151.3(3)	101(46)
X-Ray[b]	154.2(55)	147.2(30)	132.2(14)	151.9(2)	—
MINDO/3	154.5	149.9	135.6	153.0	109(–)[a]
(Theor.-X)	1.5	3.4	4.1	1.7	—
(Theor.-X_{Th})	0.5	2.7	3.4	1.1	—

[a] Fixed. [b] Corrected for thermal motion.

Table 4. Relative energy and torsion angle of the energetically most favourable conformations of the four (ethylthio)bullvalene isomers as computed by MINDO/3.

Isomer	ΔE/kJ mol^{-1}	τ/°	σ/°
O_B	2.1	270	−195
O_C	0	120	173
C	19.7	270	166
B	30.6	300	−174

rearrangement of the thermodynamically most stable O_C into the less stable O_B isomer is energetically favoured compared with the rearrangement into the identical O_C isomer, is confirmed by the theoretical data.

In summary, we have shown that the theoretical calculations based on the force fields, MINDO/3, and MNDO approximation levels are in close agreement with the experimentally determined geometries of the molecules and their thermodynamic and kinetic stabilities.

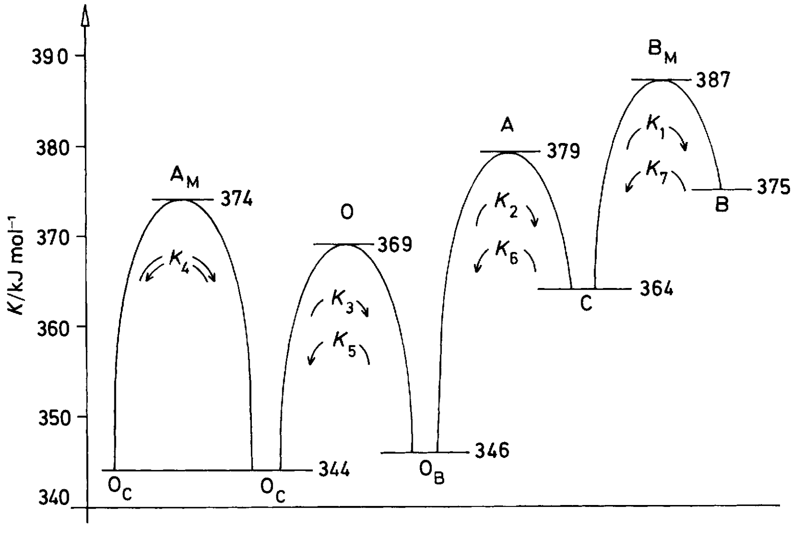


Figure 8. Total-energy profile of the valence tautomerism of (ethylthio)bullvalene.

Experimental

The n.m.r. spectra were obtained on a Bruker WH 270 Fourier transform spectrometer. Field/frequency locking was maintained by ^2H locking on the solvent signal. The free induction decays were digitized and accumulated on an Aspect 2000 computer. Typically 16 f.i.d.s were accumulated with a repetition time of 6 s. The proton chemical-shift scale was referenced to internal $SiMe_4$. The sample temperature was calibrated using the temperature-dependent chemical-shift differences in methanol and glycol.

Crystal Data.—The *X*-ray diffraction data were collected at room temperature. When exposed to *X*-rays, the crystals of (ethylthio)bullvalene decomposed rapidly at this temperature. They were totally destroyed after 50–60 h; however, during this time all necessary measurements could be carried out on one crystal, dimensions 0.3 × 0.3 × 0.3 mm: space group tetragonal $I\bar{4}$; cell dimensions $a = 1\,759.4(4)$ $c = 645.5(3)$ pm, $V_c = 1.9981(6) \times 10^9$ pm^3, $\rho_x = 1.265$ g cm^{-3}, $Z = 8$; linear absorption coefficient (Cu-K_α radiation, $\lambda = 454.18$ pm Å) 23.42 cm^{-1}.

Data Collection, Structure Analysis, and Refinement.—Data collection was made on a Stoe four-circle diffractometer (Cu-K_α radiation, Ni filter, ω–2θ scan mode). 967 Independent reflections [including 25 less thans, $I < 2\sigma(I)$] were measured in the range $5° < 2\theta < 128°$. The rapid crystal decay (by 50% at the end of the measurement) was monitored *via* two reference reflections and rescaled. Structure determination was made using direct methods (MULTAN[12]) and later confirmed by a Patterson search program IMPAS.[13] Least squares refinements were executed with anisotropic thermal parameters for S and C and isotopic temperature factors for the hydrogens, which were all located from a difference synthesis (*X*-ray program system[14]). A weighting scheme was used that made $w\Delta F$ almost independent of F_o and $\sin\theta$. Convergence was achieved at $R = 0.043$ ($R_w = 0.056$). The final fractional co-ordinates and an isotropic equivalent[15] of the anisotropic temperature factors are listed in Table 1; bond angles are in Table 2. Complete lists of atomic and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.*

Acknowledgements

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* For details of the crystallographic data deposition scheme, see 'Instructions for Authors (1989),' *J. Chem. Soc., Perkin Trans. 2*, Issue 1, p. xvii, paragraph **4**.