Crystal Structure,† Ultraviolet Spectrum, and Electronic Structure of a Strongly Twisted Push–Pull Ethylene, approaching an Amidinium–Vinylogous Dithioate Zwitterion

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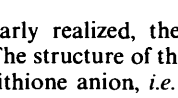
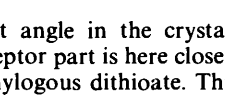
The crystal structure of 1,3-dibenzyl-2-(4,4-dimethyl-2,5-bisthioxocyclohexylidene)imidazolidine (**2**) shows a twist of 80.8(5)° about the inter-ring bond, which has a length of 1.482(6) Å. The near orthogonality of the donor and acceptor parts of this formal push–pull ethylene makes the structure approach that of a zwitterion, as evidenced by bond lengths indicating strong electron delocalization. The acceptor part approaches a vinylogous dithioate structure, the donor part an amidinium system. The u.v. spectrum shows an $n \longrightarrow \pi^*$ and a $\pi \longrightarrow \pi^*$ transition, at 511 and 417.5 nm, respectively; according to CNDO/S calculations these are located entirely in the [S–C–C–C–S]$^-$ part. Two bands at shorter wavelength are ascribed to transitions from combinations of the lone-pair orbitals on the sulphur atoms to a π^* orbital in the [N–C–N]$^+$ part; this is facilitated by the near perpendicularity of the two parts of the molecule.

1,1-Diaminoethylenes with sufficiently bulky acceptor groups (A^1, A^2) on C(2), and with the 1-amino groups joined in a five- or six-membered ring and substituted with alkyl groups [see (**1**)], are strongly twisted about the double bond both in solution[1,2] and in the solid state.[3–5] The twist is maintained by stabilization of the charges in the dipolar twisted state, which markedly lowers the barrier to rotation about the C(1)–C(2) bond, and by the strong steric repulsion between the acceptor groups A^1 and A^2 and the *N*-substituents R^1 and R^2.[6]

As the twist angle approaches 90°, the π electrons of the C(1)–C(2) bond are gradually transferred to A^1–C–A^2, and the structure approaches that of a zwitterionic molecule, with the positive charge localized in an amidinium-type structure and the negative charge in a stabilized carbanion structure. The perpendicular state simulates the transition state to rotation about the C=C bond in a normal push–pull ethylene. We report here the structure and properties of a compound (**2**) where this is nearly realized, the twist angle in the crystal being 80.8(5)°. The structure of the acceptor part is here close to that of a 1,3-dithione anion, *i.e.* a vinylogous dithioate. This compound, 1,3-dibenzyl-2-(4,4-dimethyl-2,5-bisthioxocyclohexylidene)imidazolidine, was synthesized according to Scheme 1.



(**1**) *n* = 2 or 3



(**2**)

Experimental

2-(4,4-*Dimethyl*-2,5-*dioxocyclohexylidene*)-1,3-*dithiolane* (**3**).—This was prepared according to the general method of Gompper and Töpfl[7] from dimedone, CS_2, NaH, and ethylene dibromide in dry Me_2NCHO, as yellow prisms (70% yield), m.p. 188—190 °C, δ_H (60 MHz; $CDCl_3$) 1.07 (6 H, s), 2.52 (4 H, s), and 3.36 (4 H, s).

1,3-*Dibenzyl*-2-(4,4-*dimethyl*-2,5-*dioxocyclohexylidene*)-*imidazolidine* (**4**).—The dithiolane (**3**) was refluxed in toluene for 12 h with 1 equiv. of *N,N'*-dibenzylethylenediamine. The product gave pale yellow prisms (57% yield), m.p. 190—193 °C (from xylene), δ_H (60 MHz; $CDCl_3$) 1.08 (6 H, s), 2.37 (4 H, s), 3.55 (4 H, s), 4.50 (4 H, s), and 7.37 (10 H, s); *m/z* (70 eV) 388 (7%), 371 (4), 297 (20), 132 (22), 105 (25), 91 (100), 83 (6), 77 (8), 65 (20), and 56 (12).

1,3-*Dibenzyl*-2-(4,4-*dimethyl*-2,5-*bisthioxocyclohexylidene*)-*imidazolidine* (**2**).—Reaction of (**4**) with 2,4-dianisyl-1,3,2,4-dithiadiphosphetane 2,4-disulphide (the Lawesson reagent[8]) for 4 h in toluene at 100 °C gave a crude product, which was purified by chromatography on silica with ether–light petroleum (3:1) to give orange prisms of (**2**) (44% yield), m.p. 224—225 °C, δ_H (60 MHz; $CDCl_3$) 1.07 (6 H, s), 2.85 (4 H, s), 3.59 (4 H, s), 4.47 (4 H, s), and 7.43 (10 H, s); *m/z* (70 eV) 420 (26%), 387 (58), 329 (30), 132 (18), 105 (26), 91 (100), 65 (25), and 56 (24).

The u.v.–visible spectrum of (**2**) was recorded using a Cary 219 spectrophotometer.

The CNDO/S-CI calculations were performed on a simplified model (**5**), retaining the essential bond lengths and angles from the experimental structure of (**2**). The program[9] is parametrized specifically for sulphur compounds and includes *d* orbitals on sulphur.

Crystal Structure of Compound (**2**).—*Crystal data.* $C_{25}H_{28}N_2S_2$, $M = 420.0$, monoclinic, $a = 11.685(2)$, $b = 9.892(2)$, $c = 20.864(3)$ Å, $\beta = 102.15(1)°$, $V = 2\,357.8$ Å^3, $D_m = 1.175$ g cm^{-3}, $Z = 4$, $D_c = 1.183$ g cm^{-3}, $F(000) = 896.0$, μ(Mo-K_α) = 1.98 cm^{-1}, space group $P2_1/c$, λ(Mo-K_α) = 0.7107 Å, $T = 293$ K.

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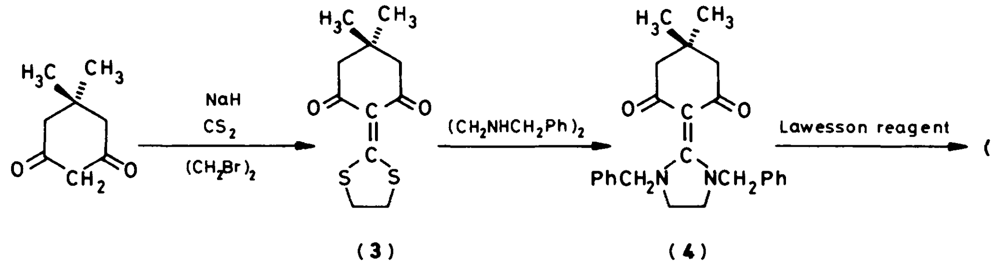
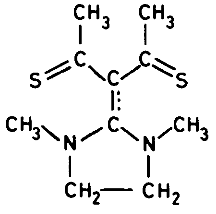
† *Supplementary data available* (SUP 56337, 7 pp.): thermal parameters. For details of Supplementary Publications see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1985, Issue 1. Structure factors are available from the editorial office on request.



Scheme 1.



(5)

Crystallographic measurements. Single crystals of the title compound were obtained from toluene. Intensity data were collected on a Nonius CAD4F-11M diffractometer using graphite-monochromated Mo-K_α (λ = 0.7107 Å) radiation in the $\omega/2\theta$ mode with a scan speed of 1° min^{-1} up to the θ limit of 23.5°.

The stability and orientation of the crystal were monitored by measuring the standard reflections after every hour; the orientation was checked after every 150 reflections. The three monitored standard reflections (2,0,0, 0,2,0, and 0,0,4) showed only statistical variations with ±5%. Out of a total of 3 879 reflections only 1 067 reflections were significant, $|F_o| \geqslant 3\sigma(|F_o|)$. The cell parameters were determined accurately by the least-squares analysis of 20 reflections. Corrections were applied for Lorentz and polarization factors but not for absorption.

Structure analysis. The structure was solved using the direct methods program MULTAN-80.[10] A few cycles of block-diagonal least-squares isotropic refinement of the non-hydrogen atoms converged to R 0.132. The program originally due to Shiono[11] was used. Full-matrix refinement (SHELX-76[12]) for the anisotropic temperature factors of the non-hydrogen atoms converged to R 0.064. Hydrogen atoms were located from a difference Fourier map at stereochemically reasonable positions. Full-matrix refinement of a scale factor, positional and anisotropic thermal parameters for the non-hydrogen atoms, and positional and isotropic temperature factors of hydrogen atoms converged to R 0.030. The function minimized was $\Sigma\omega(|F_o| - |F_c|)^2$ where $\omega = k/\sigma^2(F_o) + g|F_o|^2$ with $k = 1.6982$ and $g = 0.000\,02$. The final difference map showed no peak greater than 0.2 e Å^{-3}. Atomic scattering factors were taken from International Tables.[13]

The bond lengths within the phenyl rings tend to be less than the standard value of 1.394 Å but the standard deviation is as much as 0.015 Å. In the absence of corrections for librational motion about the C(12)–C(14) and C(13)–C(20) bonds, one might expect the bond length to be shorter than the normal value. There is no evidence for disorder of these groups in the crystal lattice.

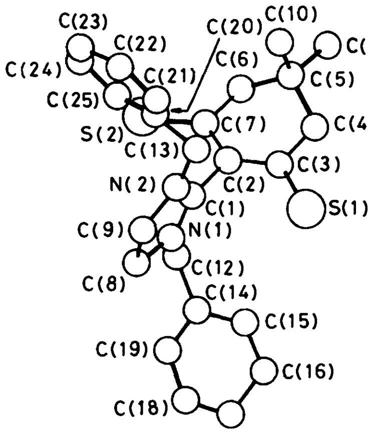


Figure 1. A perspective view of the molecule viewed down the *b* axis[16]

Table 1. Final positional (fractional) parameters for non-hydrogen atoms (× 10^4) (e.s.d.s in parentheses)

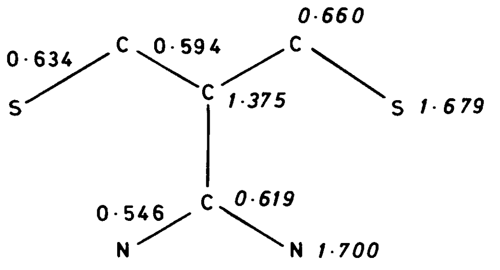
Atom	*x*	*y*	*z*
S(1)	−14(1)	2 340(1)	2 728(1)
S(2)	2 043(1)	3(2)	931(1)
C(2)	1 111(4)	1 098(5)	1 896(2)
C(3)	995(4)	1 317(5)	2 528(2)
C(4)	1 817(5)	572(7)	3 063(3)
C(5)	2 981(4)	169(6)	2 902(2)
C(6)	2 705(6)	−546(7)	2 249(3)
C(7)	1 920(4)	220(5)	1 714(2)
C(10)	3 644(8)	−878(10)	3 432(4)
C(11)	3 721(7)	1 391(9)	2 863(5)
C(12)	−1 034(5)	−94(6)	995(3)
C(13)	1 331(7)	4 033(8)	1 526(4)
C(14)	−2 259(5)	−167(6)	1 106(3)
C(15)	−2 516(7)	311(8)	1 670(4)
C(16)	−3 662(11)	260(10)	1 734(6)
C(18)	−4 273(8)	−712(10)	728(5)
C(17)	−4 528(9)	−223(11)	1 298(6)
C(19)	−3 143(6)	−704(8)	636(4)
C(20)	2 117(5)	4 586(6)	1 106(3)
C(21)	2 443(6)	5 912(7)	1 163(3)
C(22)	3 197(6)	6 442(8)	799(4)
C(23)	3 634(6)	5 639(8)	369(4)
C(24)	3 300(7)	4 322(9)	311(4)
C(25)	2 553(6)	3 803(7)	683(4)
N(1)	−633(4)	1 308(5)	986(2)
N(2)	475(4)	3 095(5)	1 183(2)
C(1)	311(5)	1 821(6)	1 360(2)
C(9)	−473(6)	3 515(7)	642(3)
C(8)	−1 194(6)	2 253(7)	485(3)

Discussion

A perspective view of the molecule, with the numbering of atoms, is shown in Figure 1. Positional co-ordinates of non-

Table 2. Interatomic distances (Å) (standard deviations in parentheses)

C(1)–C(2)	1.482(6)	C(13)–C(20)	1.501(11)
C(1)–N(1)	1.312(7)	N(2)–C(13)	1.439(9)
C(1)–N(2)	1.337(7)	C(14)–C(15)	1.358(11)
C(2)–C(3)	1.371(7)	C(14)–C(19)	1.373(9)
C(2)–C(7)	1.394(7)	C(15)–C(16)	1.374(16)
C(3)–C(4)	1.503(7)	C(16)–C(17)	1.302(15)
C(3)–S(1)	1.672(5)	C(17)–C(18)	1.372(18)
C(4)–C(5)	1.521(8)	C(18)–C(19)	1.374(13)
C(5)–C(6)	1.510(8)	C(20)–C(21)	1.364(9)
C(5)–C(10)	1.548(10)	C(20)–C(25)	1.353(10)
C(5)–C(11)	1.499(10)	C(21)–C(22)	1.381(11)
C(6)–C(7)	1.493(7)	C(22)–C(23)	1.376(11)
C(7)–S(2)	1.683(5)	C(23)–C(24)	1.359(12)
C(8)–C(9)	1.503(9)	C(24)–C(25)	1.382(12)
C(8)–N(1)	1.450(8)	C(9)–N(2)	1.466(8)
C(12)–C(14)	1.498(8)	N(1)–C(12)	1.466(8)



Scheme 2. (π electron densities italicized)

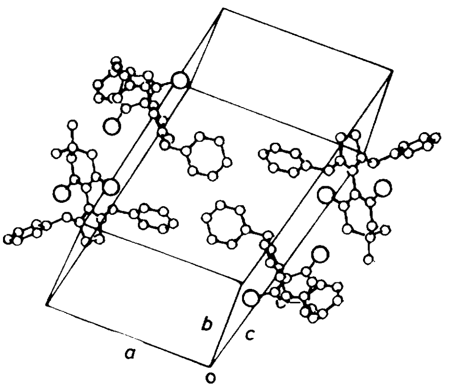


Figure 2. Packing of the molecules in the unit cell

Table 3. Selected bond and torsion angles (°) and r.m.s. deviations (Å) from least-squares planes

N(1)–C(1)–N(2)	110.6(4)	C(8)–N(1)–C(12)	121.5(4)
C(1)–N(1)–C(8)	112.0(5)	C(8)–C(9)–N(2)	103.3(5)
C(1)–N(1)–C(12)	126.1(4)	C(9)–N(2)–C(13)	122.3(5)
C(1)–N(2)–C(9)	110.5(5)	C(9)–C(8)–N(1)	103.4(5)
C(1)–N(2)–C(13)	126.5(5)	C(12)–C(14)–C(15)	120.6(5)
C(1)–C(2)–C(3)	118.4(4)	C(12)–C(14)–C(19)	120.5(6)
C(1)–C(2)–C(7)	116.9(4)	C(14)–C(15)–C(16)	118.0(8)
C(2)–C(3)–S(1)	123.6(3)	C(14)–C(19)–C(18)	120.3(8)
C(2)–C(3)–C(4)	117.4(5)	C(15)–C(16)–C(17)	125.1(12)
C(2)–C(7)–S(2)	123.0(3)	C(16)–C(17)–C(18)	117.2(11)
C(2)–C(7)–C(6)	117.3(4)	C(17)–C(18)–C(19)	120.6(8)
S(1)–C(3)–C(4)	119.0(4)	C(13)–C(20)–C(21)	119.6(6)
C(3)–C(4)–C(5)	115.2(5)	C(13)–C(20)–C(25)	122.2(6)
C(4)–C(5)–C(6)	106.9(4)	C(20)–C(21)–C(22)	121.1(7)
C(4)–C(5)–C(10)	110.6(5)	C(21)–C(22)–C(23)	120.5(7)
C(5)–C(6)–C(7)	114.7(5)	C(22)–C(23)–C(24)	118.2(8)
C(6)–C(5)–C(11)	110.2(6)	C(23)–C(24)–C(25)	120.6(8)
C(6)–C(7)–S(2)	119.8(4)		

Torsion angles:

N(1)–C(1)–C(2)–C(3)	−99.4(6)
N(1)–C(1)–C(2)–C(7)	79.6(7)
N(2)–C(1)–C(2)–C(3)	82.1(6)
N(2)–C(1)–C(2)–C(7)	−98.9(6)
C(8)–N(1)–C(12)–C(14)	−63.9(7)
C(9)–N(2)–C(13)–C(20)	−66.9(8)

Least-squares planes:

Plane 1

$$0.7186X - 0.3026Y - 0.6261Z = 2.4534$$

Atom	Deviation (Å)
N(1)	−0.040(4)
N(2)	0.042(4)
C(1)	0.003(5)
C(12)	0.028(6)
C(13)	−0.068(8)

C(2) from the above plane 0.038(4) Å

Plane 2

$$-0.6430X - 0.7617Y - 0.0795Z = 1.4251$$

Atom	Deviation (Å)
C(2)	−0.009(5)
C(3)	−0.011(5)
C(7)	0.023(6)
S(1)	0.000(1)
S(2)	−0.000(2)

C(1) from the above plane −0.017(6) Å

hydrogen atoms are listed in Table 1. Table 3 gives relevant bond and torsion angles and least-squares planes. The bond lengths (Table 2) are in good agreement with the presumed zwitterionic structure. The C(1)–C(2) bond is 1.482(6) Å, near the length of a normal single bond of C(sp^2)–C(sp^2) type.

In 2-isopropylidene-1,1,7,7,9,9-hexamethyl-3,5,10,11-tetrathiadispiro[3.1.3.2]undecane-8-thione the C=S length is 1.600(6) Å.[14] More recently a C=S bond of 1.636(9) Å has been observed, in thiobenzophenone.[15] The former system does not show any delocalization of the C=S bond whereas the latter does to a small extent. However, the S(1)–C(3) and S(2)–C(7) lengths of 1.672(5) and 1.683(5) Å, respectively, in (**2**) show definite delocalization. The C(2)–C(3) and C(2)–C(7) distances of 1.371(7) and 1.394(7) Å are short, also indicating significant electron delocalizaton.

In the donor part of the molecule, the C(1)–N(1) and C(1)–N(2) bond lengths of 1.312(7) and 1.337(7) Å, respectively, are rather short in comparison with the value of 1.452(2) Å reported for an N–C(sp^2) bond. These effects, and the presumed charge delocalization, are qualitatively reproduced by the π electron densities and π bond orders calculated by the CNDO/S method (Scheme 2). The S(1)–C(3)–C(2)–C(7)–S(2) group (the vinylogous dithioate ion) is nearly planar (Table 3, plane 2). In the C(12)–N(1)–C(1)–N(2)–C(13) group (the amidinium ion; plane 1), the deviations from planarity are larger, implying slight pyramidality at C(1) and at the nitrogen atoms.

The u.v. spectrum of (**2**) (Table 4) can be interpreted with the aid of the CNDO/S calculation. The weak band at 511 nm is assigned to an $n \longrightarrow \pi^*$ transition in the $[\text{S–C–C–C–S}]^-$ system, originating in the antisymmetric combination of the sulphur lone pairs, n_-, in agreement with a hypsochromic shift observed with increasing solvent polarity. A similar transition

Table 4. Experimental and calculated transitions for compound (**2**) in the visible–u.v. region

	Experimental			Calculated		
Solvent	$\lambda_{max.}$/nm	ε	f^a	$\lambda_{max.}$/nm	f^a	Assignment
CH_2Cl_2–Hexane						
1:1	505	260	0.0014	506.7	0.001	$n_- \longrightarrow \pi^*$ in S=C–C–C=S
5:95	511	266	0.0014			
				482.2	0.000 02	$n_+ \longrightarrow \pi^*$ in S=C–C–C=S
0.2:99.8	422	39 000 (sh)	0.292	387.8	0.301	$\pi \longrightarrow \pi^*$ in S=C–C–C=S
	417.5	40 800				
				363.9	0.000 122	From π in S=C–C–C=S to π* in N–C–N
	286	3 060	0.039	295.7	0.023	From n_- to π* in N–C–N
	235	14 000	0.185	265.3	0.162	From n_+ to π* in N–C–N

[a] Oscillator strength.

with slightly higher energy is predicted to occur from the corresponding symmetric lone-pair orbital, n_+, but is not observed, probably owing to low intensity or to overlap with another band. The strong band at 417.5 nm is assigned to a $\pi \longrightarrow \pi^*$ transition in the $[S–C–C–C–S]^-$ system. No transition corresponding to the shoulder at 422 nm is predicted, but this may be described as vibrational fine structure. At lower energies the calculations predict one transition at 296 nm from n_- to π* in the $[N–C–N]^+$ system, and one at 265 nm from n_+ to the same π* orbital. The calculated intensities agree well and the transition energies reasonably well with bands at 286 and 235 nm. The near orthogonality of the two parts of the molecule makes these transitions allowed by through-space interaction; they would have been forbidden in a planar analogue. We will investigate this effect further, using other model systems.

Acknowledgements

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