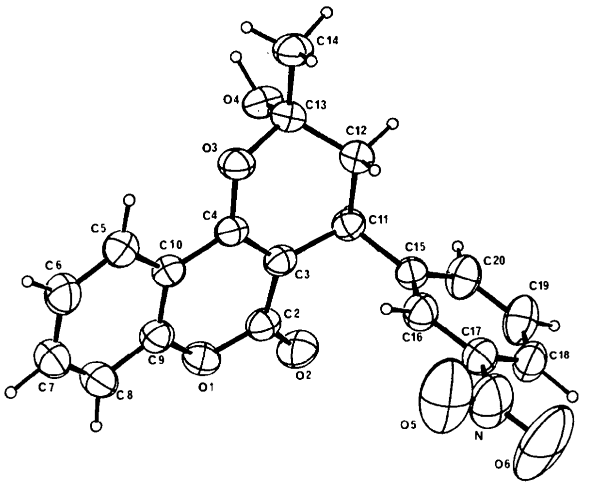

Fig. 1. A drawing of (I) showing the *A* molecule with 50% probability ellipsoids for the non-H atoms.

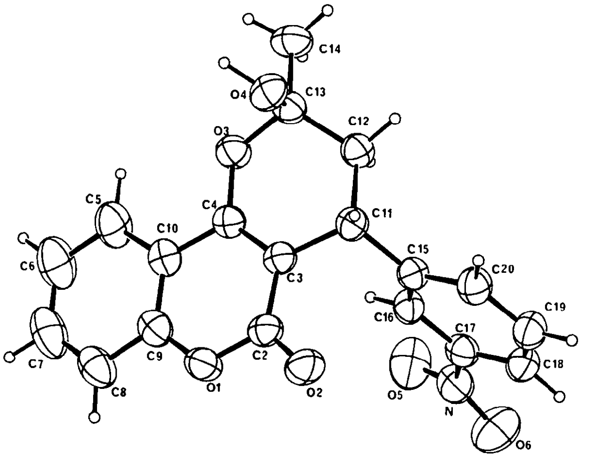

Fig 2. A drawing of (I) showing the *B* molecule with 50% probability ellipsoids for the non-H atoms.

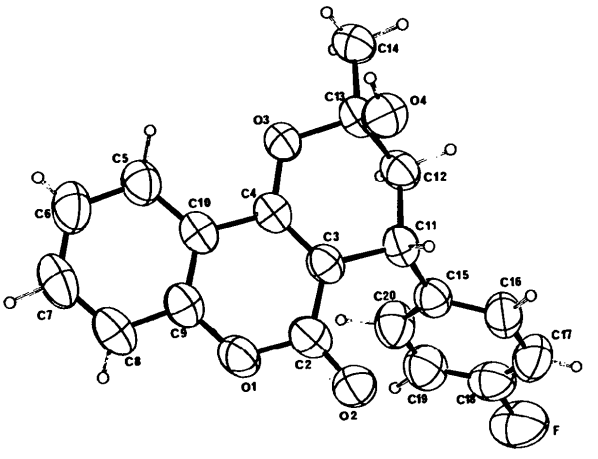

Fig. 3. A drawing of (II) with 50% probability ellipsoids for the non-H atoms.

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Structure of [1,1′:4′(*trans*),1″:4″(*trans*),1‴-Quatercyclohexane]-1″,4′-diamine

By Claus Krieger, Elfriede M. Will and Franz A. Neugebauer*

Max-Planck-Institut für medizinische Forschung, Abteilung Organische Chemie, Jahnstr. 29, D-6900 Heidelberg, Federal Republic of Germany

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Abstract. $C_{24}H_{44}N_2$, $M_r = 360{\cdot}63$, triclinic, $P\bar{1}$, $a = 6{\cdot}024\,(1)$, $b = 10{\cdot}763\,(2)$, $c = 17{\cdot}159\,(3)$ Å, $\alpha = 78{\cdot}54\,(2)$, $\beta = 81{\cdot}97\,(2)$, $\gamma = 90{\cdot}00\,(2)^\circ$, $V = 1079{\cdot}1\,(6)$ Å^3, $Z = 2$, $D_x = 1{\cdot}111$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo }K\alpha) = 0{\cdot}594$ cm^{-1}, $F(000) = 404$, $T = 295$ K, $R = 0{\cdot}049$ for 2674 unique observed reflections $[I \geq 2\sigma(I)]$. The crystal structure shows an equatorial alignment of all four cyclohexane rings and confirms the axial position of both amino groups. In the crystal there are two independent molecules: *A* with a 'parallel' alignment of all cyclohexane rings, showing a twist angle between central

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* To whom correspondence should be addressed.

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and terminal ring planes of only 1°, and *B* in which the two terminal cyclohexanes are rotated by 63° relative to the central part of the molecule.

Introduction. In the course of a program to synthesize dinitroxide spin labels with the main axis of the zero-field splitting tensor parallel to the longitudinal axis *z* of the molecule (Will, 1989; for a corresponding biverdazyl probe see Meier, Blume, Ohmes, Neugebauer & Kothe, 1982), the crystal structure of the title compound has been determined. This investigation was carried out in order to establish clearly the structure of the predominant isomer obtained by oxidative coupling of 4-nitrobicyclohexyl and subsequent reduction of the 1″,4′-dinitro[1,1′:4′,1″:4″,1‴-quatercyclohexane]s formed in the reaction. Only [1,1′:4′(*trans*),1″:4″(*trans*),1‴-quatercyclohexane]-1″,4′-diamine leads to an imidazolidine-1,3-dioxyl of required geometry.

Experimental. Needle-shaped colourless crystals, m.p. 544–546 K, obtained by recrystallization from toluene; approximate crystal dimensions 0·1 × 0·1 × 0·3 mm. Enraf–Nonius CAD-4 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation; $\theta/2\theta$ scanning technique. Lattice parameters determined from least-squares fit using 30 reflections (θ range: 12–16°); 5340 unique reflections measured in the range $2 \leq \theta \leq 28{\cdot}3°$, max. $(\sin\theta)/\lambda = 0{\cdot}671$ Å^{-1}, $0 < h < 7$, $-14 < k < 14$, $-21 < l < 22$; 2674 [$I \geq 2\sigma(I)$] used for structure solution and refinement. Three standard reflections, intensity variation max. 5%. Lorentz and polarization corrections were applied. The structure was solved by analysis of a Patterson map. Full-matrix least squares minimized $\sum w(\Delta F)^2$. H atoms refined with isotropic temperature factors, all other atoms refined anisotropically, for 411 variables, $R = 0{\cdot}049$, $wR = 0{\cdot}052$, $w = [\sigma^2(F) + 0{\cdot}005\,\sigma(F^2)]^{-1}$, max. $\Delta/\sigma = 0{\cdot}1$; residual electron density in final difference map $-0{\cdot}21 < \Delta\rho < 0{\cdot}18$ e Å^{-3}. Atomic scattering factors and anomalous-dispersion corrections taken from *International Tables for X-ray Crystallography* (1974). Programs used were those of B. A. Frenz & Associates Inc. (1982).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for non*-H *atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
Molecule *A*				
C(1)	0·0786 (3)	0·0903 (2)	0·7824 (1)	3·28 (5)
C(2)	0·3081 (3)	0·0802 (2)	0·8108 (1)	4·65 (7)
C(3)	0·2953 (4)	0·0778 (2)	0·9003 (1)	5·78 (8)
C(4)	0·1830 (4)	0·1934 (2)	0·9228 (1)	6·16 (8)
C(5)	−0·0472 (4)	0·2063 (2)	0·8963 (1)	5·69 (8)
C(6)	−0·0382 (4)	0·2053 (2)	0·8073 (1)	4·34 (6)
C(1′)	0·0907 (3)	0·0934 (2)	0·6921 (1)	2·83 (5)
C(2′)	−0·1396 (3)	0·1002 (2)	0·6646 (1)	3·34 (6)
C(3′)	−0·1335 (3)	0·1028 (2)	0·5759 (1)	3·09 (5)
C(4′)	−0·0133 (3)	−0·0087 (2)	0·5470 (1)	2·59 (5)
C(5′)	0·2165 (3)	−0·0185 (2)	0·5764 (1)	3·18 (5)
C(6′)	0·2067 (3)	−0·0199 (2)	0·6660 (1)	3·46 (6)
N(4′)	−0·1432 (3)	−0·1284 (2)	0·5822 (1)	4·07 (5)
Molecule *B*				
C(1)	0·4780 (3)	0·5650 (2)	0·7938 (1)	3·59 (6)
C(2)	0·6208 (4)	0·6836 (2)	0·7879 (1)	4·58 (7)
C(3)	0·6474 (4)	0·7075 (2)	0·8707 (1)	6·00 (8)
C(4)	0·4221 (4)	0·7150 (2)	0·9207 (1)	6·56 (8)
C(5)	0·2752 (4)	0·5988 (2)	0·9268 (1)	5·79 (8)
C(6)	0·2519 (4)	0·5771 (2)	0·8432 (1)	4·66 (7)
C(1′)	0·4570 (3)	0·5273 (2)	0·7133 (1)	3·23 (5)
C(2′)	0·6805 (3)	0·4977 (2)	0·6685 (1)	4·00 (6)
C(3′)	0·6515 (3)	0·4453 (2)	0·5945 (1)	3·76 (6)
C(4′)	0·5242 (3)	0·5335 (2)	0·5353 (1)	2·77 (5)
C(5′)	0·3071 (3)	0·5719 (2)	0·5806 (1)	3·49 (6)
C(6′)	0·3402 (3)	0·6227 (2)	0·6554 (1)	3·61 (6)
N(4′)	0·6642 (3)	0·6484 (2)	0·4980 (1)	4·83 (5)

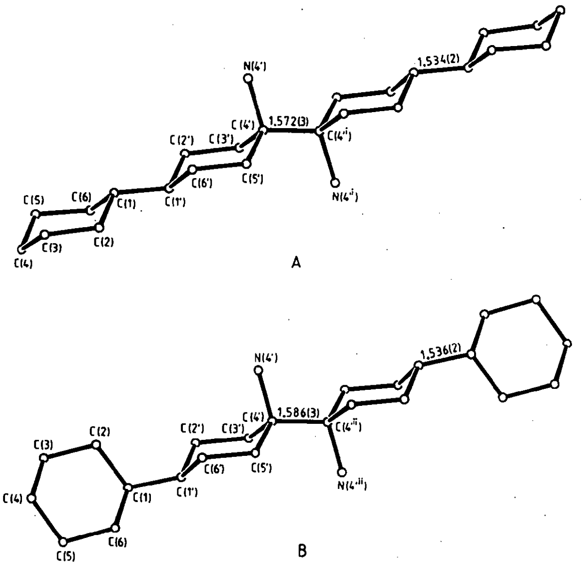

Fig. 1. Views of the conformations *A* and *B* showing the labelling scheme and the bond distances (Å) between the cyclohexane components. Symmetry code: (*A*) (i) $x' = -x$, $y' = -y$, $z' = 1 - z$; (*B*) (ii) $x' = 1 - x$, $y' = 1 - y$, $z' = 1 - z$.

Discussion. The title compound crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules in the unit cell which lie on different centres of symmetry. These conformations, *A* and *B*, and the atomic labelling scheme are given in Fig. 1. Symmetry-related atoms have been indicated by (i) for *A* and by (ii) for *B*. Final atomic coordinates with equivalent isotropic temperature factors, and comparative molecular geometry are given in Tables 1 and 2 respectively.*

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and molecular dimensions involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52093 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Comparative molecular geometry* (Å *and* °) *for molecules A and B with e.s.d.'s in parentheses*

	Molecule *A*	Molecule *B*
(*a*) Bond lengths		
C(1)—C(2)	1·526 (2)	1·518 (2)
C(1)—C(6)	1·528 (2)	1·521 (2)
C(1)—C(1′)	1·534 (2)	1·536 (2)
C(2)—C(3)	1·522 (3)	1·523 (3)
C(3)—C(4)	1·507 (3)	1·512 (3)
C(4)—C(5)	1·517 (3)	1·509 (3)
C(5)—C(6)	1·523 (3)	1·524 (3)
C(1′)—C(2′)	1·524 (2)	1·521 (2)
C(1′)—C(6′)	1·519 (2)	1·525 (2)
C(2′)—C(3′)	1·513 (2)	1·519 (2)
C(3′)—C(4′)	1·532 (2)	1·534 (2)
C(4′)—C(4′^{i})	1·572 (3)	1·586 (3)
C(4′)—C(5′)	1·535 (2)	1·526 (2)
C(4′)—N(4′)	1·481 (2)	1·479 (2)
C(5′)—C(6′)	1·527 (2)	1·528 (1)
(*b*) Valence angles		
C(2)—C(1)—C(6)	108·9 (2)	109·2 (2)
C(2)—C(1)—C(1′)	113·0 (2)	115·2 (2)
C(6)—C(1)—C(1′)	112·4 (2)	112·9 (2)
C(1)—C(2)—C(3)	112·8 (2)	111·4 (2)
C(2)—C(3)—C(4)	111·5 (2)	111·3 (2)
C(3)—C(4)—C(5)	110·5 (2)	111·9 (2)
C(4)—C(5)—C(6)	112·1 (2)	110·2 (2)
C(1)—C(6)—C(5)	113·5 (2)	112·2 (2)
C(1)—C(1′)—C(2′)	112·7 (2)	113·3 (2)
C(1)—C(1′)—C(6′)	113·3 (2)	115·2 (2)
C(2′)—C(1′)—C(6′)	107·5 (2)	108·0 (2)
C(1′)—C(2′)—C(3′)	114·0 (2)	112·0 (2)
C(2′)—C(3′)—C(4′)	114·2 (2)	113·3 (2)
C(3′)—C(4′)—C(4′^{ii})	111·4 (2)	110·6 (2)
C(3′)—C(4′)—C(5′)	108·0 (2)	109·2 (2)
C(3′)—C(4′)—N(4′)	110·0 (2)	109·5 (2)
C(4′^{ii})—C(4′)—C(5′)	110·9 (2)	111·3 (2)
C(4′^{ii})—C(4′)—N(4′)	107·9 (2)	107·0 (2)
C(5′)—C(4′)—N(4′)	108·5 (2)	109·2 (2)
C(4′)—C(5′)—C(6′)	114·0 (2)	113·8 (2)
C(1′)—C(6′)—C(5′)	113·6 (2)	111·5 (2)
(*c*) Selected torsion angles		
C(1′)—C(1)—C(2)—C(3)	179·7 (3)	−175·4 (3)
C(1′)—C(1)—C(6)—C(5)	−178·5 (3)	173·1 (3)
C(2)—C(1)—C(1′)—C(6′)	56·2 (3)	−63·6 (3)
C(6)—C(1)—C(1′)—C(2′)	−57·7 (3)	−172·3 (3)
C(6)—C(1)—C(1′)—C(6′)	179·9 (3)	62·7 (3)
C(1)—C(2)—C(3)—C(4)	−57·2 (3)	−55·8 (3)
C(4)—C(5)—C(6)—C(1)	53·8 (3)	56·6 (3)
C(1)—C(1′)—C(2′)—C(3′)	−179·7 (3)	173·0 (3)
C(1)—C(1′)—C(6′)—C(5′)	179·2 (3)	−174·6 (3)
C(1′)—C(2′)—C(3′)—C(4′)	55·8 (3)	56·7 (3)
C(2′)—C(3′)—C(4′)—C(5′)	−50·9 (3)	−50·7 (3)
C(3′)—C(4′)—C(5′)—C(6′)	50·8 (3)	50·7 (3)
C(2′)—C(3′)—C(4′)—N(4′)	67·4 (3)	68·8 (3)
N(4′)—C(4′)—C(5′)—C(6′)	−68·5 (3)	−69·0 (3)
C(4′)—C(5′)—C(6′)—C(1′)	−55·7 (3)	−56·4 (3)
C(3′)—C(4′)—C(4′^{i})—C(5′^{i})	−59·7 (3)	−58·4 (3)
C(3′)—C(4′)—C(4′^{i})—N(4′^{i})	59·0 (3)	60·9 (3)
N(4′)—C(4′)—C(4′^{i})—N(4′^{i})	180·0	180·0
C(5′)—C(4′)—C(4′^{i})—N(4′^{i})	−61·3 (3)	−60·8 (3)
C(2′)—C(3′)—C(4′)—C(4′^{i})	−172·9 (3)	−173·6 (3)
C(6′)—C(5′)—C(4′)—C(4′^{i})	173·2 (3)	173·2 (3)

Symmetry codes: (i) $x' = -x$, $y' = -y$, $z' = 1 - z$; (ii) $x' = 1 - x$, $y' = 1 - y$, $z' = 1 - z$.

In *A* and *B* the cyclohexane rings all adopt the expected chair conformation. All cyclohexane segments are *trans* to each other and occupy equatorial positions on each connected ring. This arrangement is similar to that of 1,1′:4′,1″-*trans*-tercyclohexane (Sasvári & Párkányi, 1976). The C(sp^3)—C(sp^3) bonds within the cyclohexane rings vary only from 1·507 (3) to 1·535 (2) Å with a mean value of 1·522 (7) Å. Most of the C—C—C angles are about 112°, as is normal for cyclohexane rings. Significant deviations are found for C(2)—C(1)—C(6), C(2′)—C(1′)—C(6′) and C(3′)—C(4′)—C(5′) ≃ 109° in *A* and *B*, and additionally in *B* for C(2)—C(1)—C(1′) and C(1)—C(1′)—C(6′) ≃ 115°. In *B* these deviations are obviously connected with short intramolecular contacts between C(2)···C(2′) 3·123 (2), C(2)···C(6′) 3·181 (2) and C(6)···C(6′) 3·131 (2) Å. Both amino groups at the central carbons are located in axial positions. The central bonds, C(4′)—C(4′^{i}) in *A* and C(4′)—C(4′^{ii}) in *B*, are longer [1·572 (2) and 1·586 (2) Å respectively] than the C(1)—C(1′) distances [1·534 (2) and 1·536 (2) Å respectively] in agreement with the degree of substitution at these carbons (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The C—N bond lengths and the C—C—N bond angles lie in the range of aliphatic amines.

The conformations *A* and *B* differ in the arrangement of the outer cyclohexanes. *A* shows a 'parallel' alignment of all cyclohexane rings. The angle between the central [C(2′), C(3′), C(5′), C(6)] and terminal ring plane [C(2), C(3), C(5), C(6)] is only 1°, and the torsion angle C(6)—C(1)—C(1′)—C(6′) = 179·9 (3)°. In *B* the outer cyclohexane rings are twisted by 63° relative to the central ones, also shown by C(6)—C(1)—C(1′)—C(6′) = 62·7 (3)°. The degree of rotation of the outer ring of *B* relative to its position in *A* is 61°. The reason for the conformation of *B* is not obvious. A short intermolecular contact is only found for N(4′)*A*···N(4′)*B* [$-1+x$, $-1+y$, z] 3·325 (2) Å (see Fig. 2). A simulation of a 'parallel' arrangement of the outer cyclohexane ring relative to the central ring of *B* produces short intermolecular contacts: C(5*)···C(5*) [$1-x$, $1-y$, $2-z$] 2·72, C(4*)···C(6*)

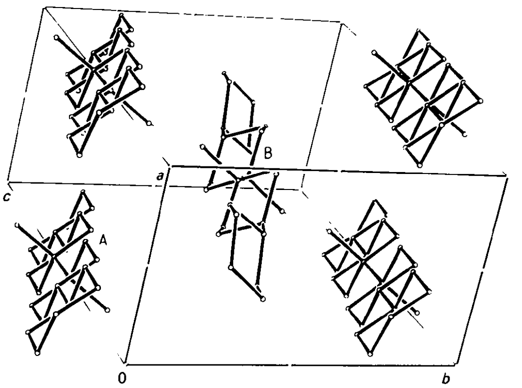

Fig. 2. Molecular packing in the unit cell, also showing the short intermolecular contact between N(4′)*A* and N(4′)*B*.

2·98, and C(3*)···C(5*) 3·09 Å. These intermolecular contacts are only little affected by variations of the three Euler angles ($\leq 5°$) with a fixed position of *B* in the unit cell. Therefore we assume that only by conformational variation can an optimal packing be achieved. Fig. 2 shows the packing arrangement in the unit cell. The central segments of both conformations are nearly parallel to each other and approximately related by a 180° rotation about [001] followed by a $\frac{1}{2}, \frac{1}{2}, 0$ translation.

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Structures of *N*,*N*′-Dimethyl-2,2′-dithiodibenzamide and 2-(Benzylsulfinyl)-*N*-methylbenzamide. Intramolecular Nonbonding S···O Interaction

By Fujiko Iwasaki,* Nobuhiko Toyoda and Norimasa Yamazaki

Department of Applied Physics and Chemistry, The University of Electro-Communications,
Chofu-shi, Tokyo 182, *Japan*

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Abstract. $C_{16}H_{16}N_2O_2S_2$ (I), $M_r = 332{\cdot}45$, monoclinic, $C2/c$, $a = 18{\cdot}680\,(4)$, $b = 4{\cdot}9246\,(7)$, $c = 18{\cdot}733\,(5)$ Å, $\beta = 112{\cdot}43\,(2)°$, $V = 1593{\cdot}0\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}386$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 0{\cdot}327$ mm^{-1}, $F(000) = 696$, $T = 293$ K, $R = 0{\cdot}036$ for 1625 observed reflections. $C_{15}H_{15}NO_2S$ (II), orthorhombic, $Pcab$, $a = 16{\cdot}148\,(3)$, $b = 12{\cdot}428\,(2)$, $c = 14{\cdot}233\,(2)$ Å, $V = 2857{\cdot}5\,(7)$ Å^3, $Z = 8$, $D_x = 1{\cdot}271$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 0{\cdot}213$ mm^{-1}, $F(000) = 1152$, $T = 293$ K, $R = 0{\cdot}055$ for 2292 observed reflections. Molecule (I) with a crystallographic twofold axis shows short intramolecular S···O contacts of 2·896 (1) Å. The molecules form ribbon-like intermolecular hydrogen bonds between amide groups. The N···O distance is 2·818 (2) Å. For molecule (II) the intramolecular S···O distance is 2·717 (3) Å. The molecules are linked by the hydrogen bonds between the sulfinyl oxygen and the N—H of the amide group, forming a zigzag chain. The N···O length is 2·851 (4) Å.

Introduction. It is well known that some S atoms in compounds such as σ-sulfuranes and thiathiophthenes show hypervalency (Musher, 1969). The characteristic features of the hypervalent bonds in these compounds are as follows:

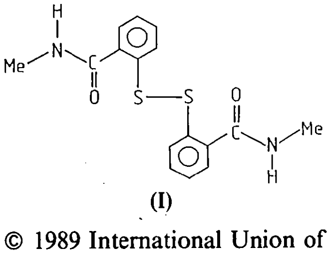
(1) A tetravalent or divalent S atom forms an X···S···Y bond system with electronegative groups X and Y, where $X = Y$ or not.

(2) These S···X and S···Y bonds are longer than usual S—X and S—Y single-bond distances, respectively, but they are much shorter than the sum of the van der Waals radii.

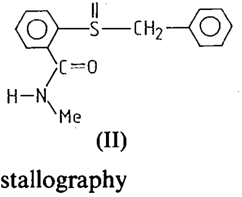
(3) These bonds correspond to Pauling's bond order 0·5 and are more liable to changes in bond length if the molecule is perturbed to some degree.

(4) The X···S···Y arrangement is almost linear.

Besides such typical hypervalent bonds, S···O, S···N or S···halogen nonbonding intramolecular contacts are often observed in some organic sulfur compounds (Iwasaki & Akiba, 1985; Iwasaki, 1986; Iwasaki & Masuko, 1986). For the title compounds the electron-attracting benzamide group is expected to have a short intramolecular contact with the S atom. We determined the crystal structures of these two compounds in order to study hypervalency of the S atoms.



(I)



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* To whom all correspondence should be addressed.

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