

4458 measured reflections 2 standard reflections
 4182 independent reflections every 98 reflections
 2066 reflections with intensity decay: 5%
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.101$

Refinement

Refinement on F^2 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $R[F^2 > 2\sigma(F^2)] = 0.072$ $\Delta\rho_{\text{max}} = 0.23 \text{ e } \text{\AA}^{-3}$
 $wR(F^2) = 0.121$ $\Delta\rho_{\text{min}} = -0.37 \text{ e } \text{\AA}^{-3}$
 $S = 1.225$ Extinction correction: none
 4117 reflections Scattering factors from
 343 parameters *International Tables for*
 H atoms constrained *Crystallography* (Vol. C)
 $w = 1/[\sigma^2(F_o^2) + (0.0683P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

Table 1. Selected geometric parameters (\AA , $^\circ$)

N1—C2	1.446 (4)	C5—C6	1.352 (5)
N2—C4	1.432 (4)	C7—C8	1.395 (4)
N3—C6	1.438 (4)	C7—C13	1.415 (4)
C1—C6	1.489 (4)	C8—C9	1.384 (4)
C1—C2	1.493 (4)	C9—C10	1.378 (5)
C2—C3	1.367 (5)	C10—C11	1.393 (5)
C3—C4	1.385 (4)	C11—C12	1.391 (5)
C4—C5	1.385 (4)	C12—C13	1.376 (4)
C3—C2—C1	124.0 (3)	C8—C7—C13	131.1 (3)
C2—C3—C4	120.3 (3)	C10—C9—C8	130.4 (3)
C3—C4—C5	120.6 (3)	C9—C10—C11	131.4 (4)
C6—C5—C4	120.6 (3)	C12—C11—C10	129.1 (3)
C5—C6—C1	124.6 (3)	C12—C13—C7	132.7 (3)
C13—O8—C1—O7	-3.7 (3)	C1—O8—C13—C7	3.8 (3)
C7—O8—C1—O8	2.2 (3)	O7—C7—C13—O8	-2.4 (3)
C1—O7—C7—C13	-0.1 (3)		

Table 2. Intramolecular contact distances (\AA) and van der Waals radii

		Radius†
O1...C7	2.816 (4)	3.00
O1...C13	2.777 (4)	3.00
O2...H3	2.369 (5)	2.45
O3...H3	2.428 (5)	2.45
O4...H5	2.395 (4)	2.45
O5...H5	2.359 (4)	2.45
O6...C7	2.896 (4)	3.00
O6...C13	2.959 (4)	3.00

† van der Waals radii are taken from Zefirov & Zorky (1989).

The slightly high value of R_1 is attributed to the limited quality of available crystals.

Data collection: P3 (Siemens, 1989). Cell refinement: P3. Data reduction: PROFIT (Strel'tsov & Zavodnik, 1989). Program(s) used to solve structure: SHELXTL-Plus (Sheldrick, 1994). Program(s) used to refine structure: SHELXTL-Plus. Molecular graphics: SHELXTL-Plus. Software used to prepare material for publication: SHELXTL-Plus.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1362). Services for accessing these data are described at the back of the journal.

References

- Artamkina, G. A., Egorov, M. P. & Beletskaya, I. P. (1982). *Chem. Rev.* **82**, 427–459.
- Borbulevych, O. Ya., Shishkin, O. V., Kovalevsky, A. Yu., Atroschenko, Yu. M., Alifanova, E. N., Gitis, S. S., Kaminsky, A. Ya. & Tarasova, E. Yu. (1998). *Monatsh. Chem.* **129**, 467–472.
- Buncel, E., Dust, J. M. & Terrier, F. (1995). *Chem. Rev.* **95**, 2261–2280.
- Furmanova, N. G., Struchkov, Yu. T., Kompan, O. E., Budarina, Z. N., Olekhovich, L. P. & Minkin, V. I. (1980). *Zh. Strukt. Khim.* **21**, 83–89.
- Knyazev, V. N. & Drozd, V. N. (1995). *Zh. Org. Khim. (Russ. J. Org. Chem.)*, **31**, 3–30.
- Kurbatov, S. V., Budarina, Z. N., Vaslyayeva, G. S., Borisenko, N. I., Knyazev, A. P., Minkin, V. I., Zhdanov, Y. A. & Olekhovich, L. P. (1997). *Russ. Chem. Bull.* **46**, 1445–1448.
- Olekhovich, L. P., Furmanova, N. G., Minkin, V. I., Struchkov, Yu. T., Kompan, O. E., Budarina, Z. N., Yudilevich, I. A. & Eryuzheva, O. V. (1982). *Zh. Org. Khim. (Russ. J. Org. Chem.)*, **18**, 465–474.
- Sheldrick, G. M. (1994). *SHELXTL-Plus*. Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1989). *P3. Program for Data Collection*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Strel'tsov, V. A. & Zavodnik, V. E. (1989). *Kristallografiya*, **34**, 1369–1375.
- Zefirov, Yu. V. & Zorky, P. M. (1989). *Usp. Khim. (Russ. Chem. Rev.)*, **58**, 713–746.

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2-Benzoyl-2-methyl-1,3-dithiane

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Abstract

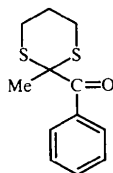
The crystal structure of the title compound, $\text{C}_{12}\text{H}_{14}\text{OS}_2$, shows a 1,3-dithiane ring adopting a chair conformation with the 2-benzoyl group orientated axially. The carbonyl-O atom lies above the heterocycle, but is asymmetrically disposed with respect to both S atoms. Thus, the conformation can mainly be discussed on the basis of electrostatic dipole–dipole attraction (anomeric effect) of the C—S and C=O dipoles, together with *exo*-orientation of the phenyl group as a consequence of its steric demand. The observed bond distances do not support an $n \rightarrow \sigma^*$ delocalization as a further reason for the axial orientation of the carbonyl group.

Comment

2-Acyl-1,3-dithianes represent important key intermediates and may, after sulfoxidation, be used as stereocon-

trol elements for a wide variety of synthetic transformations, principally involving carbonyl-group reactivity (Page *et al.*, 1996). Furthermore, chiral building blocks for the synthesis of optically active secondary alcohols and α -hydroxy ketones can be obtained directly and with high enantiomeric excess by enantioselective reduction of the basic compounds (DeNinno *et al.*, 1990). For steric reasons 2-acyl-1,3-dithianes exhibit interesting conformational behaviour with the acyl group orientated axially, as deduced from NMR spectroscopy (Juaristi *et al.*, 1986).

In the course of our investigations directed at new chiral synthons from 2-acyl-1,3-dithianes we have now carried out the crystal structure determination of the title compound, (I). As expected the 1,3-dithiane ring adopts a chair conformation. The bond distances are normal and



(I)

are similar to those found for other 2-substituted 1,3-dithianes, *e.g.* 2-phenyl-1,3-dithiane with C—S at 1.80 (3) and 1.79 Å, C—C at 1.51 (3) and 1.46 (3) Å (Kalff & Romers, 1966), 2-methyl-2-triphenylsilyl-1,3-dithiane with C—S at 1.815 (3) and 1.824 Å, C—C at 1.497 (6) and 1.505 (6) Å (Bryan *et al.*, 1978), 2-[1,3]-dithianyldiphenylphosphine oxide with C—S at 1.809 (3) and 1.810 (3) Å, C—C at 1.517 (5) Å (Juaristi *et al.*, 1984), 2-methyl-2-(4-nitrophenyl)-1,3-dithiane with C—S at 1.813 (6) and 1.820 (6) Å, average C—C 1.523 Å (Fink & Stahl, 1985) and 2-(1,3-dithian-2-ylidene-methyl)-1,3-dithiane with C—S at 1.799 (7) and 1.792 (7) Å, C—C at 1.501 (11) and 1.497 (10) Å (Dziadulewicz *et al.*, 1989); they do not differ greatly from the standard values for Csp³—S and Csp³—Csp³ [1.819 (19) and 1.530 (15) Å; Allen *et al.*, 1987]. The benzoyl group at C4 is orientated axially; its O atom lies above the heterocycle but is asymmetrically disposed with respect to both S atoms. The torsion angles S1—C4—C5—O and S2—C4—C5—O are -98.5 (2) and 24.2 (3)°, and the molecule (I) thus deviates significantly from C_s-symmetry. The bulky aryl group is orientated away from the dithiane ring and furthermore twisted with respect to the plane of the carbonyl group. The relevant torsion angles O—C5—C6—C11 and O—C5—C6—C7 are equal to -37.1 (3) and +139.6 (2)°.

The fact that the benzoyl group is orientated axially can be interpreted on the basis of the 'anomeric effect' (Eliel, 1972) and so mainly rationalized in terms of stabilization by dipole-dipole attraction of the C—S and the C=O dipoles. A second common explanation of the anomeric effect can be given in terms of delocalization of the lone pair on the endocyclic heteroatom into

the antiperiplanar (axial) adjacent polar bonds (Romers *et al.*, 1969). According to the latter interpretation, the presence of significant $n_S \rightarrow \sigma^*$ interactions should be manifested in shortened C4—S1 or C4—S2 and elongated C4—C5 distances in the axial *versus* the equatorial isomer. However, in the absence of data for the equatorial conformer of (I), no conclusion can be drawn at present as to whether these bonds are shortened with respect to those in the equatorial conformer. The C4—C5 bond distance of the title compound (I) is, at 1.536 (3) Å, only slightly elongated with respect to the relevant Csp³—C=O distance in the reference compound 1-benzoyl-4-*tert*-butyl-1-methylcyclohexane, for which a value of 1.527 (4) has been determined recently (Fu *et al.*, 1997) and for which a stereoelectronic stabilization as a consequence of the absence of heteroatoms in the ring can be strictly ruled out. Supporting this argument, it is known that stereoelectronic stabilization is indeed not valid for all types of 2-substituted 1,3-dithianes, as has been demonstrated for 1,3-dithianyldiphenylphosphine oxide, which bears an axially orientated PO group (Juaristi *et al.*, 1984). The C—P bond distance in the reference compound, *r*-2-(diphenylphosphinoyl)-*c*-4,*c*-6-dimethyl-1,3-dithiane (Juaristi *et al.*, 1984), which bears an equatorially orientated diphenylphosphinoyl group, is significantly longer than that in the axial compound, mentioned above. This observation, together with the mean S1—C2 bond lengths of both compounds, which do not show any significant difference, are thus contrary to the expectations, if an $n_S \rightarrow \sigma^*_{C-P}$ interaction made an important contribution to the axial conformation of the basic compound, *i.e.* such an interaction would have been manifested in shortened C—S and elongated C—P distances in the axial *versus* equatorial form.

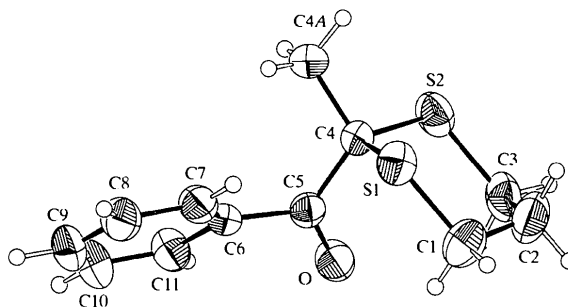


Fig. 1. Perspective drawing (ZORTEP: Zsolnai, 1993) of the title compound indicating the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

The steric crowding at C4 of (I) leads to significant alterations of the angles within the heterocycle. As compared with the structure parameters of 2-phenyl-1,3-dithiane the molecule (I) is more puckered in the C—C—C region as is indicated by the lower values for the S—C—C, C—C—C and S—C—S angles, whereas a pronounced flattening at the opposite side

of the ring is associated with the opening of the C—S—C angle to 104.90(12)°. Comparable values for the C—S—C angles of 2-phenyl-1,3-dithiane, 2-methyl-2-triphenylsilyl-1,3-dithiane, 2-[1,3]-dithianyldiphenylphosphine oxide, 2-methyl-2-(4-nitrophenyl)-1,3-dithiane and 2-(1,3-dithian-2-ylidenemethyl)-1,3-dithiane are 99.20(15) and 100.90(15)°, 102.6(2) and 101.7(2)°, average 101.3(1)°, 101.4(3) and 100.9(3)° and 101.4(4) and 100.4(3)°. Associated torsion angles C1—S1—C4—S2 and C3—S2—C4—S1 for the S—C—S moiety are -55.22(15) and 51.23(15)°; C1—C2—C3—S2 and S1—C1—C2—C3 for the C—C—C moiety are 61.9(3) and -68.5(3)°.

Experimental

The *N*-acylation of *N,O*-dimethylhydroxylamine hydrochloride was performed according to DeVoss *et al.* (1994) starting with benzoyl chloride (1.95 g, 13.9 mmol) and *N,O*-dimethylhydroxylamine hydrochloride (1.50 g, 15.4 mmol) in anhydrous trichloromethane (150 ml). The crude *N*-methoxy-*N*-methylbenzamide needs no further purification and was added, diluted in dry tetrahydrofuran (THF) (50 ml), over a period of 30 min at 188 K to a stirred solution of 2-lithio-2-methyl-1,3-dithiane in anhydrous THF. The latter compound was prepared by the method of Seebach & Corey (1975), by lithiation of a 0.5 *M* solution of 2-methyl-1,3-dithiane (2.07 g, 15.4 mmol) in anhydrous THF with a 1.6 *M* solution of *n*-butyllithium in *n*-hexane. The reaction mixture was then warmed in 3 h to 273 K and diluted with a saturated aqueous solution of ammonium chloride. After extraction with diethyl ether/dichloromethane (100 ml, 1:1) and drying over sodium sulfate, the solvents were removed under reduced pressure. The solid thus obtained was recrystallized from methanol/water (2:1) to give 2-benzoyl-2-methyl-1,3-dithiane (1.16 g, 35% yield), m.p. 371–372 K [literature 372–373 K (Page *et al.*, 1988)]. Crystals of X-ray quality were grown from the same solvent mixture.

Crystal data

C₁₂H₁₄OS₂
M_r = 238.35
 Monoclinic
*P*2₁/*n*
a = 6.056(1) Å
b = 26.822(3) Å
c = 7.713(1) Å
 β = 106.61(1)°
V = 1200.6(3) Å³
Z = 4
D_x = 1.319 Mg m⁻³
D_m not measured

Data collection

Enraf–Nonius CAD-4
 diffractometer
 ω scans

Mo *K* α radiation
 λ = 0.71073 Å
 Cell parameters from 25
 reflections
 θ = 16–18°
 μ = 0.414 mm⁻¹
T = 298(2) K
 Plate
 0.60 × 0.40 × 0.10 mm
 Colourless

Absorption correction:
 refined from ΔF (Walker
 & Stuart, 1983)
T_{min} = 0.738, *T_{max}* = 1.000
 4196 measured reflections
 2107 independent reflections

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.038
wR(*F*²) = 0.079
S = 0.999
 2107 reflections
 136 parameters
 H-atom parameters
 constrained

θ_{\max} = 25.01°
 $h = -7 \rightarrow 7$
 $k = -31 \rightarrow 0$
 $l = -9 \rightarrow 9$
 2 standard reflections
 frequency: 120 min
 intensity decay: 1%
 $w = 1/[\sigma^2(F_o^2) + (0.0339P)^2 + 0.0388P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.19 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.16 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

S1—C1	1.801(3)	C1—C2	1.511(4)
S1—C4	1.821(2)	C2—C3	1.505(4)
S2—C3	1.804(3)	C4—C4A	1.523(3)
S2—C4	1.814(2)	C4—C5	1.536(3)
C1—S1—C4	101.42(12)	C3—C2—C1	113.3(2)
C3—S2—C4	104.90(12)	C2—C3—S2	115.2(2)
C2—C1—S1	113.5(2)		
S1—C1—C2—C3	-68.5(3)	S2—C4—C5—O	24.2(3)
C1—C2—C3—S2	61.9(3)	S1—C4—C5—O	-98.5(2)
C3—S2—C4—S1	51.23(15)	O—C5—C6—C7	139.6(2)
C1—S1—C4—S2	-55.22(15)	O—C5—C6—C11	-37.1(3)

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1995).
 Cell refinement: CAD-4 EXPRESS. Data reduction: XCAD4
 (Harms, 1993). Program(s) used to solve structure: SHELXS97
 (Sheldrick, 1990). Program(s) used to refine structure:
 SHELXL97 (Sheldrick, 1997). Molecular graphics: ZORTEP
 (Zsolnai, 1993).

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Supplementary data for this paper are available from the IUCr
 electronic archives (Reference: JZ1341). Services for accessing these
 data are described at the back of the journal.

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
 Bryan, R. F., Carey, F. A., Hernandez, O. & Taylor, I. F. (1978). *J. Org. Chem.* **43**, 85–90.
 DeNinno, M. P., Perner, R. J. & Lijewski, L. (1990). *Tetrahedron Lett.* **51**, 7415–7418.
 DeVoss, J. J., Sui, Z., DeCamp, D. L., Salto, R., Babe, L. M., Craik, C. S. & Ortiz de Montellano, P. R. (1994). *J. Med. Chem.* **37**, 665–673.
 Dziadulewicz, E., Giles, M., Moss, W. O., Gallagher, T., Harmann, M. & Hursthouse, M. B. (1989). *J. Chem. Soc. Perkin. Trans. 1*, pp. 1793–1798.
 Eliel, E. L. (1972). *Angew. Chem. Int. Ed. Engl.* **11**, 739–750.
 Enraf–Nonius (1995). CAD-4 EXPRESS. Version 5.1. Enraf–Nonius, Delft, The Netherlands.

- Fink, H. & Stahl, I. (1985). *Acta Cryst.* **C41**, 151–153.
 Fu, T. Y., Leibovitch, M., Scheffer, J. R. & Trotter, J. (1997). *Acta Cryst.* **C53**, 1255–1256.
 Harms, K. (1993). *XCAD4. Program for the Reduction of CAD-4 Diffractometer Data*. University of Marburg, Germany.
 Juaristi, E., Tapia, J. & Mendez, R. (1986). *Tetrahedron*, **421**, 1253–1264.
 Juaristi, E., Valenzuela, B. A. & Valle, L. (1984). *J. Org. Chem.* **49**, 3026–3027.
 Kalf, H. T. & Romers, C. (1966). *Acta Cryst.* **20**, 490–496.
 Page, P. C. B., van Niel, M. B. & Westwood, D. (1988). *J. Chem. Soc. Perkin Trans. 1*, pp. 269–275.
 Page, P. C. B., Wilkes, R. D., Namwindwa, E. S. & Witty, M. J. (1996). *Tetrahedron*, **52**, 2125–2154.
 Romers, C., Altona, C., Buys, H. R. & Havinga, E. (1969). *Top. Stereochem.* **4**, 39–97.
 Seebach, D. & Corey, E. J. (1975). *J. Org. Chem.* **40**, 231–237.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
 Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.
 Zsolnai, L. (1993). *ZORTEP. Program for Graphic Representation of Crystal Structures*. University of Heidelberg, Germany.

Acta Cryst. (1999). **C55**, 2182–2184

N-Benzyl-*N*-(2-iodo-4-methylphenyl)-cinnamamide and *N*-benzyl-*N*-(*p*-tolyl)-cinnamamide

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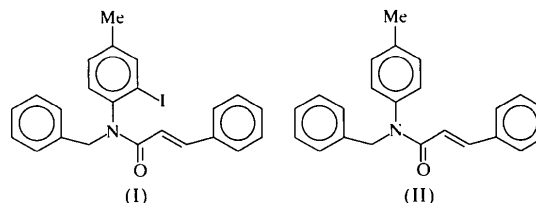
Abstract

The cinnamamide moiety in the crystals of the title compounds, C₂₃H₂₀INO, (I), and C₂₃H₂₁NO, (II), is almost planar and the benzyl ring is twisted through 60.4(4) and 63.6(1)° with respect to this moiety in (I) and (II), respectively. In the unit cell, the molecules exist as dimers joined through C—H···O hydrogen bonding.

Comment

Cinnamoyl anilides are substrates for cyclization to biologically active five-membered 2-oxindole derivatives and six-membered 2-oxyquinolines by photochemical methods. *ortho*-Iodinated anilides are used for the same reaction by electrochemical methods. Interest lies in the

synthetic potential of the title iodinated compound, *N*-benzyl-*N*-(2-iodo-4-methylphenyl)cinnamamide, (I), and those of other acyclamides which react with a wide range of nucleophilic compounds and which therefore present new possibilities in the synthesis of heterocyclic compounds (Augustin *et al.*, 1980). We have undertaken the X-ray structure analyses of the two title compounds, (I) and *N*-benzyl-*N*-(*p*-tolyl)cinnamamide, (II), as an extension of studies of the molecular packing of cinnamamide derivatives.



The bond lengths and angles of the cinnamamide group in (I) and (II) are comparable with the analogues *N*-methyl-2'-nitrocinnamamide (Subramanian *et al.*, 1999) and *N*-(4-chloro-2-iodophenyl)-*N*-methylcinnamamide (Renganayaki *et al.*, 1999) reported by our group, and with other reported values (Iwamoto & Kashino, 1990; Iwamoto *et al.*, 1989). The C—I distance in (I) is comparable with the values of the *para*-substituted compounds [2.088(4) (Elmali & Elerman, 1997) and 2.085(4) Å (Banerjee *et al.*, 1994)]. The widening of the C1—C7—C8 angle [127.8(3)° in (I) and 128.5(3)° in (II)] is due to the intramolecular repulsion of C2 and C8 [C2···C8 = 3.034(5) Å in (I) and 3.045(4) Å in (II)] and perhaps also to the attractive intramolecular force between C7 and O10 [C7···O10 = 2.818(5) in (I) and 2.788(3) Å in (II)]. Structural studies reveal that the exocyclic N11 atom is *sp*² hybridized despite forming three valence bonds. The inner angle at C22 is smaller [C21—C22—C23: 118.6(3)° in (I) and 117.1(3)° in (II)] than the *sp*² angle commonly observed at methyl-substituted C-atom positions (Dominicano *et al.*, 1975).

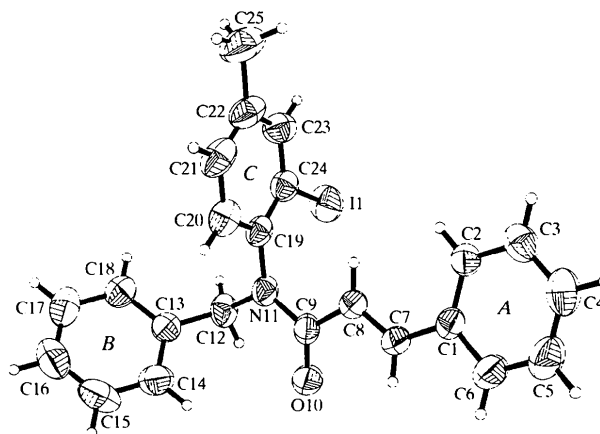


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as spheres of arbitrary radii.