Fig. 2. Paire stéréo montrant l'organisation des ponts hydrogène.

Ponts hydrogène

Les distances entre atomes d'oxygène confirment l'existence de ponts hydrogène. Comme chaque groupe OH participe à une de ces liaisons, on observe au total 12 ponts hydrogène différents. Leurs caractéristiques géométriques sont décrites dans le Tableau 3. Les contacts O···O qui ne sont pas particulièrement courts varient dans l'intervalle 2,691 (4) à 2,832 (4) Å et ont une moyenne de 2,743 Å. Dans le cas de l'isomère de position, *tert*-butyl-4 cyclohexanediol-1,2-(1*r*,2*c*,3*t*) (Brice *et al.*, 1972) les contacts O···O sont légèrement plus longs (intervalle 2,77 à 2,90 Å, moyenne 2,828 Å) alors que pour le *m*-crésol, ils sont généralement plus courts [intervalle 2,66 (1) à 2,73 (1) Å, moyenne 2,69 Å].

Les quatre molécules (III), (IV), (V) et (VI) forment avec leurs homologues centrosymétriques un amas, lié par pont hydrogène et centré sur un centre d'inversion de la maille. Cet amas est connecté à un autre groupe formé des molécules (I) et (II) et celles qui sont déduites par un autre centre de symétrie de la maille. Cet assemblage complexe est présenté sous forme d'une paire stéréo en Fig. 2. Cette organisation tridimensionnelle n'a aucun rapport avec celle de l'isomère de position (Brice *et al.*, 1972).

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The Tetra-1-naphthoide*–Cyclohexanone (1/2) Clathrate

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Abstract. $C_{44}H_{24}O_8 \cdot 2C_6H_{10}O$, $M_r = 877 \cdot 0$, triclinic, $P\bar{1}$, $a = 10 \cdot 383$ (2), $b = 13 \cdot 849$ (4), $c = 17 \cdot 516$ (4) Å, $\alpha = 103 \cdot 58$ (1), $\beta = 101 \cdot 40$ (1), $\gamma = 102 \cdot 70$ (1)°, $V = 2304$ (1) Å^3, $Z = 2$, $D_x = 1 \cdot 264$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, μ(Mo $K\alpha$) $= 0 \cdot 807$ cm^{-1}, $F(000) = 920$, room temperature, $R = 0 \cdot 113$ for 2820 observed reflections. The host lattice is characterized by channels running parallel to the a axis which accommodate two independent guest cyclohexanone molecules. The bond lengths and angles of the host are similar to those found for the unsolvated form, but the dihedral angles between

pairs of opposite naphthalene planes differ. The two guest molecules have chair and flattened-chair conformations and are disordered.

Introduction. Tetra-1-naphthoide (1) is able to enclathrate different guest molecules varying in shape and size from chloroform to naphthalene. Some of our results are reported in Table 1. All the clathrates of (1) which have been investigated so far are isomorphous and crystallize in the triclinic system with the exception of the complexes with benzene and tetracyanoethylene. Also, the stability of the different clathrates depends markedly on the structure of the guest molecule. The crystal structure of the unsolvated form of (1) has been recently determined (Gerdil & Bernardinelli, 1985). The present paper is concerned with the crystal structure of the clathrate with cyclohexanone as guest molecule.

Experimental. Colourless crystal of average dimensions $0.3 \times 0.4 \times 0.5$ mm mounted inside a Lindemann-glass capillary tube together with a small amount of mother liquor to prevent decomposition of clathrate. Philips PW1100 diffractometer, graphite-monochromated Mo $K\alpha$; cell dimensions from 40 reflections ($9 < \theta < 12°$); data collection: $\sin\theta/\lambda < 0.52$ Å^{-1} ($0 < h < 10$, $-13 < k < 13$, $-17 < l < 16$), ω–2θ scans, ω-scan angle $1.2°$; 5016 reflections, 2820 unique with $|F_o| > 3\sigma(F_o)$, 2196 unobserved. Lorentz–polarization correction (no absorption or extinction correction). Distribution of data $\langle E^2-1\rangle = 1.046$ indicated centrosymmetric space group. Structure solved by direct methods (MULTAN80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); block-diagonal least squares using $|F|$ values; rigid-body refinement of guest molecules. Parameters refined: one scale factor, positional parameters and anisotropic temperature factors for non-H atoms of host, isotropic temperature factors for H atoms of host [positions of H atoms calculated with $d(C—H) = 1.08$ Å], translations and rotations of rigid-body guests

with overall isotropic temperature factor. $R = 0.113$, $wR = 0.126$, $S = 13.03$, $w(F) = \exp[18.0(\sin\theta/\lambda)^2]$ (Dunitz & Seiler, 1973); max. and av. $|\Delta|/\sigma$ values for non-H atomic parameters 0.004 and 0.002; max. and min. heights in final difference electron density map 0.56 and 0.49 e Å^{-3}; atomic scattering factors for non-H atoms from Cromer & Mann (1986), for H atoms from Stewart, Davidson & Simpson (1965), anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974); all calculations performed with a local version of XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), MM2 (Allinger, 1977), PARST (Nardelli, 1983) and ORTEPII (Johnson, 1976). Atomic parameters are listed in Table 2.*

Discussion.
Molecular structure

The geometries of the host molecule and the guest model are shown in Figs. 1 and 2, respectively. Because it is on a general position, the host molecule is asymmetric, but its average bond distances and valence angles are similar, within experimental error, to those found for the 4-symmetrical unsolvated form (Gerdil & Bernardinelli, 1985). A significant conformational difference, however, occurs between the dihedral angles subtended by the two pairs of opposite naphthalene mean molecular planes. In the present structure, the angles are 61.6 (3) and 69.2 (3)° between the planes (i)–(iii) and (ii)–(iv), respectively, whereas the unique angle of the unsolvated molecule is 66.8° (two opposite naphthalene planes are related here by a pseudo-twofold axis, Fig. 1b). The conformation of the central 16-membered ring is characterized by the torsion angles

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43598 (93 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Clathrates formed by* tetra-1-*naphthoide*

	Cyclohexanone	Chloro-cyclohexane	Chloroform	2-Bromobutyric acid	Naphthalene	Benzene	TCNE†
a (Å)	10.383 (2)	10.494 (3)	10.585 (3)	10.398 (1)	10.264	14.17	10.670 (2)
b (Å)	13.849 (4)	14.239 (3)	13.519 (4)	13.900 (2)	13.963	14.59	12.418 (2)
c (Å)	17.516 (4)	17.685 (5)	17.589 (8)	17.488 (4)	17.291	16.43	14.038 (2)
α (°)	103.58 (1)	105.55 (1)	94.46 (2)	91.56 (2)	76.08	65.6	92.11 (1)
β (°)	101.40 (1)	104.05 (1)	106.61 (2)	106.36 (1)	79.12	75.5	99.19 (1)
γ (°)	102.70 (1)	99.46 (1)	104.26 (2)	108.66 (1)	73.18	86.5	98.31 (1)
V (Å³)	2304.4	2394.1	2152.1	2278.6	2104.0	2678.6	1814.1
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P1$ or $P\bar{1}$	$P\bar{1}$
Host/guest ratio	1/2	1/2	—	—	—	—	2/1
Stability*	n	n	vn	s	s	vn	s

Other possible guest molecules: tetrahydrofuran, mesitylene, toluene, trichloroethylene, ethyl acetate, carbon tetrachloride.
* s stable, n unstable, vn very unstable.
† TCNE = tetracyanoethylene.

Table 2. *Final fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$)

E.s.d.'s are given in parentheses.

$U_{eq} = \frac{1}{3}$ (trace of orthogonalized U_{ij} matrix).

	x	y	z	U_{eq}
C(1)	6416 (10)	3882 (7)	5922 (5)	58 (4)
C(2)	5001 (11)	3701 (8)	5552 (6)	64 (4)
C(3)	3957 (11)	3560 (9)	5963 (6)	69 (4)
C(4)	2633 (11)	3428 (10)	5592 (7)	78 (5)
C(5)	2249 (12)	3383 (11)	4759 (8)	84 (5)
C(6)	3224 (11)	3500 (9)	4331 (6)	72 (4)
C(7)	4600 (10)	3656 (7)	4709 (5)	57 (4)
C(8)	5623 (12)	3780 (9)	4284 (6)	71 (5)
C(9)	6931 (12)	3955 (10)	4663 (6)	73 (5)
C(10)	7382 (11)	3995 (8)	5510 (6)	62 (4)
C(11)	8882 (10)	4177 (9)	5840 (6)	64 (4)
O(1)	9655 (8)	4050 (8)	5444 (5)	83 (4)
O(2)	9249 (7)	4532 (5)	6670 (4)	63 (3)
C(12)	10622 (11)	4628 (8)	7043 (6)	66 (4)
C(13)	11547 (11)	5613 (8)	7259 (6)	64 (4)
C(14)	11184 (14)	6451 (10)	7069 (8)	89 (6)
C(15)	12124 (17)	7389 (12)	7258 (10)	102 (7)
C(16)	13445 (18)	7525 (15)	7663 (11)	119 (8)
C(17)	13891 (16)	6727 (15)	7889 (9)	109 (7)
C(18)	12941 (12)	5739 (11)	7690 (7)	85 (5)
C(19)	13329 (15)	4911 (12)	7896 (8)	91 (6)
C(20)	12353 (12)	3969 (10)	7672 (7)	78 (5)
C(21)	10992 (10)	3809 (9)	7239 (6)	66 (4)
C(22)	10110 (12)	2728 (9)	7025 (6)	70 (5)
O(3)	10373 (9)	2063 (7)	7306 (6)	91 (4)
O(4)	8960 (7)	2545 (5)	6414 (4)	65 (3)
C(23)	8030 (11)	1567 (8)	6172 (6)	64 (4)
C(24)	8044 (13)	884 (10)	5451 (6)	74 (5)
C(25)	8985 (15)	1148 (10)	4994 (7)	85 (6)
C(26)	8928 (23)	427 (18)	4263 (10)	128 (10)
C(27)	8031 (29)	−532 (22)	3995 (13)	156 (12)
C(28)	7072 (25)	−822 (15)	4412 (13)	140 (10)
C(29)	7080 (17)	−132 (10)	5167 (9)	96 (6)
C(30)	6105 (17)	−371 (11)	5608 (10)	106 (7)
C(31)	6090 (16)	360 (10)	6300 (9)	93 (6)
C(32)	7037 (12)	1345 (9)	6578 (6)	70 (5)
C(33)	6830 (11)	2081 (8)	7281 (6)	64 (4)
O(5)	5813 (10)	1978 (8)	7491 (6)	104 (4)
O(6)	7959 (7)	2885 (5)	7675 (4)	62 (3)
C(34)	7826 (11)	3678 (9)	8301 (6)	70 (5)
C(35)	8287 (12)	3598 (11)	9106 (6)	76 (5)
C(36)	8794 (14)	2789 (10)	9244 (7)	83 (6)
C(37)	9221 (20)	2772 (16)	10035 (9)	120 (9)
C(38)	9118 (19)	3503 (16)	10698 (9)	111 (8)
C(39)	8645 (18)	4295 (15)	10569 (7)	110 (8)
C(40)	8187 (13)	4378 (12)	9767 (7)	83 (6)
C(41)	7717 (14)	5207 (13)	9607 (7)	95 (6)
C(42)	7325 (13)	5271 (10)	8829 (8)	82 (5)
C(43)	7359 (10)	4492 (8)	8148 (6)	62 (4)
C(44)	6969 (11)	4650 (10)	7340 (5)	69 (5)
O(7)	6835 (12)	5466 (7)	7241 (5)	98 (5)
O(8)	6720 (6)	3788 (5)	6712 (3)	57 (3)

Guest cyclohexanone
Molecule A

O(9)	2565	2448	1237	250*
C(45)	1963	1708	1407	
C(46)	2356	700	1261	
C(47)	2484	328	2025	
C(48)	1183	268	2325	
C(49)	877	1322	2503	
C(50)	726	1708	1746	

Molecule B

O(10)	6831	251	1856	230*
C(51)	6243	−643	1482	
C(52)	6827	−1525	1607	
C(53)	6785	−2251	787	
C(54)	5337	−2621	211	
C(55)	4826	−1700	75	
C(56)	4842	−964	884	

* Average temperature factor for rigid body.

reported in Table 3. The short O⋯O and O⋯C contacts in the central macrocyclic ring cause considerable internal strain (Table 4). The electron density obtained from difference syntheses (Fig. 3) at the sites of the guest molecules reveals smeared maxima leading to chemically unsatisfactory geometries for the cyclohexanone molecules A and B. In consequence, an 'ideal' geometry was calculated by the force-field method (MM2; Allinger, 1977) and included as a rigid component in the model. The final orientation of the rigid guest molecule in each site is compared with that of the observed molecules as shown in Fig. 3. The geometry and the orientation of the observed A molecule and of the rigid-body model are very similar; on the other hand, the observed B conformation appears much more flattened than the 'ideal' chair conformation. This may be due to a large molecular motion of the loosely packed guests or/and multipositional disorder in the channels. The lack of structural accuracy in localizing the guest molecules is
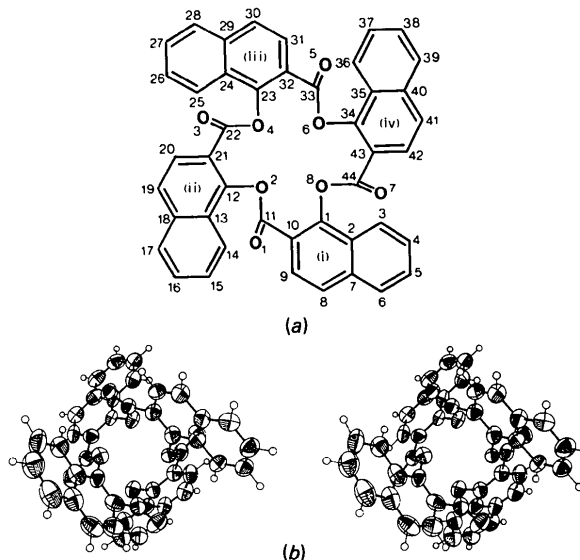

Fig. 1. The tetra-1-naphthoide host molecule: (a) atom-numbering scheme; (b) ORTEPII (Johnson, 1976) stereoview. Ellipsoids of 50% probability are used for non-H atoms; the H atoms are indicated by spheres of 0·1 Å radius.
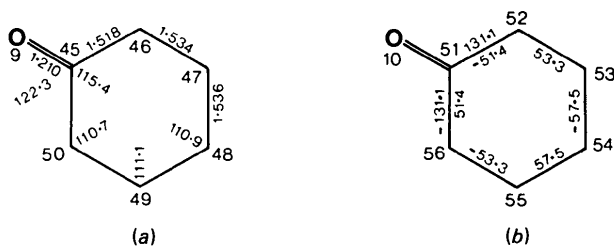

Fig. 2. Atom-numbering scheme and 'ideal' geometry (MM2; Allinger, 1977) for the lower-energy conformation of cyclohexanone: (a) bond lengths (Å) and angles (°); (b) torsion angles (°).

the most likely reason for the relatively high value of the *R* factor. Various attempts to refine the disordered structure were unsuccessful. The lower-energy chair conformation adopted by cyclohexanone is consistent with the relatively large cavity, which does not impose strong non-bonded interactions upon the included guests.

Table 3. *Endocyclic torsion angles* (°) *in the central 16-membered ring of the host molecule*

E.s.d.'s are given in parentheses.

C(1) C(10) C(11)–O(2)	–18·7 (16)	C(23)–C(32)–C(33)–O(6)	–21·1 (16)
C(10) C(11) O(2) C(12)	173·9 (8)	C(32)–C(33)– O(6)–C(34)	174·0 (9)
C(11) O(2) C(12) C(21)	–88·0 (12)	C(33)- O(6)–C(34)- C(43)	–85·6 (13)
O(2) C(12) C(21) -C(22)	7·0 (17)	O(6)–C(34)–C(43)–C(44)	–1·0 (17)
C(12) C(21) C(22) O(4)	16·7 (16)	C(34)–C(43)–C(44)–O(8)	18·1 (16)
C(21) C(22) O(4) C(23)	178·3 (9)	C(43)–C(44)–O(8)–C(1)	–176·6 (8)
C(22) O(4) C(23) C(32)	85·3 (13)	C(44)–O(8)–C(1)–C(10)	98·2 (11)
O(4) C(23) C(32) C(33)	0·8 (17)	O(8)–C(1)–C(10)–C(11)	–8·7 (17)

Table 4. *Selected non-bonded intramolecular distances* (Å) *in the host molecule*

E.s.d.'s are given in parentheses.

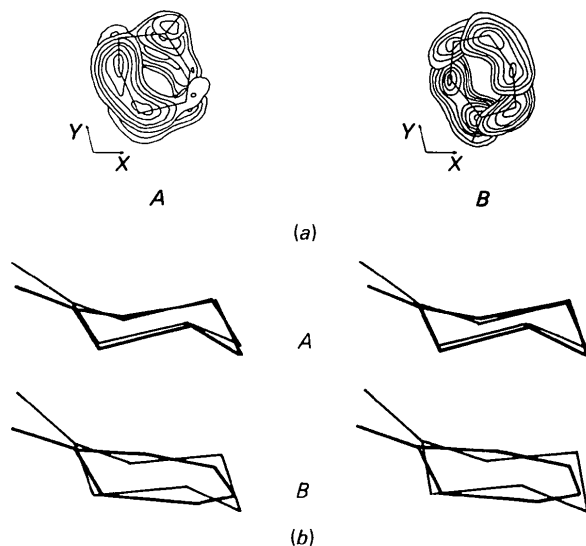|	Clathrate	Unsolvated host*	Sum of van der Waals radii
O(2)···O(4)	2·622 (10)	2·626 (3)	3·04
O(2)···O(8)	2·624 (9)		
O(4)···O(6)	2·611 (11)		
O(6)···O(8)	2·628 (10)		
O(2)···C(22)	2·987 (16)	2·773 (4)	3·09
O(4)···C(33)	2·961 (14)		
O(6)···C(44)	2·986 (15)		
O(8)···C(11)	2·979 (13)		

* Gerdil & Bernardinelli (1985).

Fig. 3. Cyclohexanone guest molecules *A* and *B*. (*a*) Compound view of difference maps parallel to the *ab* plane: lowest contour at 40 e Å⁻³, contour interval 10 e Å⁻³, and (*b*) stereoviews of the superposition of the molecules obtained from *ΔF* syntheses (heavy line) with the rigid-body guest model in its final orientations.
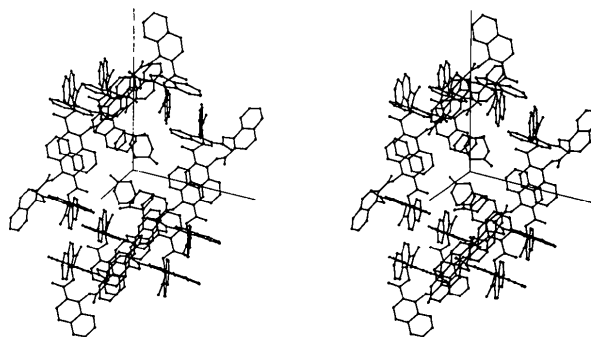

Fig. 4. Stereoscopic view (*ORTEP*II; Johnson, 1976) of the channel along the *a* axis; the origin of the crystal system and the directions of the crystallographic axes are also indicated. H atoms are omitted.

Crystal packing

The cyclohexanone molecules are arranged in centro-symmetric pairs in channels running parallel to the *a* axis. Guest molecules *A* are accommodated close to the centre of symmetry at 0,0,0 with the closest approach occurring between H(46*a*) and H(50*e*) at 3·39 Å (van der Waals contact 2·34 Å). Molecules *B* are related through the centre of symmetry at $\frac{1}{2}$,0,0 and the closest contact involves the H(55*a*)···H(56*e*) pair separated by 2·53 Å. Two contacts shorter than the sum of van der Waals radii are observed between molecules *A* and *B*: 2·19 Å [H(46*e*)···H(56*e*ⁱⁱ)] and 2·21 Å [H(46*e*)···H(55*a*ⁱⁱⁱ)]; all other intermolecular guest···guest distances are longer than the sum of corresponding van der Waals radii. The packing of the guest molecules inside the channel is shown in Fig. 4. Short host···host interatomic contacts appear between C(21) and H(4ⁱⁱⁱ) and O(7) and H(6ⁱᵛ), 2·62 and 2·46 Å, respectively (sum of van der Waals radii: 2·79 Å for C···H, and 2·69 Å for O···H). The close contacts observed between (1) and guest *A* are H(42)···O(42ⁱᵛ) = 2·18, H(6)···H(49*e*ⁱ) = 2·18, H(38)···H(50*a*ᵛ) = 2·25 and H(15)···H(49*a*ⁱᵛ) = 2·29 Å; between (1) and guest *B*: O(5)···H(52*e*ⁱⁱ) = 2·49, O(5)···H(56*a*ⁱⁱ) = 2·68 and H(41)···H(53*e*ᵛⁱ) = 2·19 Å [symmetry code: (i) *x*, *y*, *z*; (ii) −*x*+1, −*y*, −*z*+1; (iii) *x*+1, *y*, *z*; (iv) −*x*+1, −*y*+1, −*z*+1; (v) *x*+1, *y*, *z*+1; (vi) *x*, *y*+1, *z*+1; (vii) *x*, *y*−1, *z*; (viii) 1−*x*, −*y*, −*z*].

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Structure of N-(β-Phenylpropionyl)glycine Ethyl Dithioester*

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Abstract. $C_{13}H_{17}NOS_2$, $M_r = 267 \cdot 4$, monoclinic, $P2_1/c$, $a = 11 \cdot 863$ (2), $b = 4 \cdot 821$ (1), $c = 25 \cdot 292$ (3) Å, $\beta = 90 \cdot 61$ (1)°, $V = 1446 \cdot 4$ Å^3, $Z = 4$, $D_x = 1 \cdot 228$ Mg m^{-3}, $\lambda(Cu\ K\alpha_1) = 1 \cdot 54056$ Å, $\mu(Mo\ K\alpha) = 0 \cdot 34$ mm^{-1}, $F(000) = 568$, $T = 293$ K, final $R = 0 \cdot 045_5$, $wR = 0 \cdot 051$ for 2335 unique reflections. The glycinic N and thiol S atoms are in short non-bonded contact [$2 \cdot 901$ (2) Å] as frequently observed in thioester derivatives of glycine and alanine. The $N–CH_2–C–S$(thiol) and $C–NH–CH_2–C$ torsion angles are $-18 \cdot 9$ (3) and $-75 \cdot 4$ (3)° respectively, and the dihedral angle between the phenyl ring and the amide group is $58 \cdot 9°$. A molecular-mechanics calculation indicates that this dihedral angle is $81 \cdot 9°$ in the minimum-energy conformation.

Introduction. Joint crystallographic and spectroscopic studies on various N-acylglycine and N-acylalanine dithio- and thiolesters have elucidated some structure–spectra relationships in this series of compounds (Huber, Ozaki, Pliura, Storer & Carey, 1982; Huber, Carey, Hsi, Lee & Storer, 1984; Varughese, Storer & Carey, 1984; Angus, Carey, Lee, Storer & Varughese, 1985). These correlations are used to obtain detailed information on the acyl group structure in corresponding dithioacyl papain intermediates, using the dithioester group as a resonance Raman probe. Although the resonance Raman spectra of N-benzoylglycine ethyl dithioester and of its para-substituted analogues are reasonably well understood, some aspects of the spectra of the title compound (I) were puzzling (Lee, Storer & Carey, 1983) and prompted this X-ray study. In particular, $^{13}C=S$ isotopic substitution of (I) gives a resonance Raman spectrum in CH_3CN/H_2O solution in which a peak that was expected (by comparison with the N-benzoyl

analogue) to occur near 1100 cm^{-1} is apparently split into two peaks at 1079 and 1115 cm^{-1}. Very similar behavior is observed in the spectrum of the corresponding dithioacylpapain (Storer, Lee & Carey, 1983).
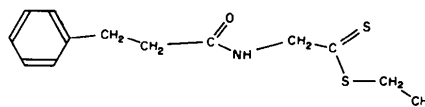
(I)

Experimental. Yellow lath-shaped crystals, grown by diffusion of hexane vapor into an ether solution of (I), were provided by Dr A. C. Storer; precession photographs indicated monoclinic symmetry, space group Pc or $P2_1/c$; specimen $0 \cdot 20 \times 0 \cdot 25 \times 0 \cdot 40$ mm; Enraf–Nonius CAD-4F diffractometer; cell dimensions from refinement of θ angles of 25 carefully-centered reflections with $30 < \theta < 44°$ using Ni-filtered Cu $K\alpha$ radiation. Intensity measurements made with Zr-filtered Mo $K\alpha$ radiation; $\omega/2\theta$ scans with $\Delta\omega = 1 \cdot 5(1 \cdot 25 + 0 \cdot 35\tan\theta)°$; three check reflections monitored after every 3000 s of X-ray exposure showed only random fluctuations; all 4184 independent reflections in the range $\theta \le 30°$ were measured; index range h 0 to 16, k 0 to 6, l -35 to 35; 2335 reflections considered observed [$I \ge 1 \cdot 50\sigma(I)$]. Lorentz–polarization corrections applied, but not absorption. Structure solved with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Intensity statistics indicated strongly that the structure was noncentrosymmetric, and therefore space group Pc was assumed for the structure solution step. However, the structure clearly conforms to $P2_1/c$ symmetry and has been refined in this space group. Non-H atoms refined first isotropically, subsequently anisotropically, all H atoms located on difference maps and refined isotropically, block-diagonal least squares, minimizing $\sum w(\Delta F)^2$.