Bull. Chem. Soc. Jpn., 56, 2922—2926 (1983)

The Crystal Structure of 11-(*p*-Bromophenyl)-11-cyano-12-phenyl-6b-(1-pyrrolidinyl)-6b,6c,11,12a-tetrahydroindeno[1'2' : 3,4]-cyclopenta[1,2-*a*]acenaphthylene Acetone Solvate

Tetsuo Uechi,* Otohiko Tsuge,† Shigeru Okita,† and Shuji Kanemasa†
College of General Education, Kyushu University 01, Ropponmatsu, Fukuoka 810
†*Research Institute of Industrial Science, and Department of Molecular Science and Technology, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University 86, Kasuga, Kasugashi, Fukuoka 816*

(Received April 4, 1983)

The title compound crystallizes in the triclinic space group $P\bar{1}$ with two fomrula units in a unit cell of dimensions; $a=11.621(3)$, $b=15.177(3)$, $c=10.229(2)$ Å, $\alpha=95.63(2)$, $\beta=105.46(2)$, and $\gamma=76.43(2)°$. The crystal structure was solved by a conventional heavy-atom method and refined by block-diagonal least-squares procedures to give a final R value of 0.050 for 3428 reflections, with $F_o>2\sigma(F_o)$, collected on a four-circle diffractometer. The bond distance shared between the acenaphthene and the cyclopentane rings is unusually long at 1.596(6) Å, which may result from the additional strain induced by the fusion of these rings. The solvent molecules are disordered in the channel composed of the main molecules.

As a part of our studies of the reaction of enamines with triafulvenes, we have recently reported that 1-(1-pyrrolidinyl)acenaphthylene reacts with 2-phenyl-2-(2,3-diphenyl-2-cyclopropenylidene)acetonitrile to give two isomeric 1 : 1 adducts.[1] This reaction was regared as the first example in which a phenyl group on the three-membered ring of methylenecyclopene had taken part in a cyclization. On the basis of chemical and spectroscopic techniques alone, the stereochemical structures of the adducts could not be elucidated unambiguously. In order to confirm the structure as well as to explore the essential features of this reaction, we have undertaken an X-ray structural study of the title main molecule (abbreviated as ICPA) which was the major product from the reaction of 1-(1-pyrrolidinyl)acenaphthylene with 2-(*p*-bromophenyl)-2-(2,3-diphenyl-2-cyclopropenylidene)acetonitrile under the same reaction conditions. The X-ray structural study was not applied to the minor product because the crystals obtained were unsuitable.

Experimental

The title compound was obtained by recrystallization from acetone as colorless prisms elongated along the c axis. The crystal used for the X-ray work was approximately triclinic in shape, with dimensions of 0.2 mm × 0.3 mm × 0.4 mm, and it was coated with nail enamel to prevent deterioration in air. The density was measured by flotation in an aqueous KI solution. Preliminary X-ray photographs showed the crystal to be triclinic. The unit-cell parameters and intensity data were measured on a Rigaku automated four-circle diffractometer with monochromated Mo $K\alpha$ radiation ($\lambda=0.71073$ Å). The unit-cell parameters were determined by a least-squares procedure using 25 reflections within the range of $23<2\theta<27°$. The crystal data are given in Table 1.

Table 1. Crystal data[a]

Formula unit	$C_{39}H_{29}N_2Br\cdot C_3H_6O$
Formula weight	663.66
Space group	$P\bar{1}$
$a=11.621$ (3) Å	$\alpha=95.63$ (2)°
$b=15.177$ (3) Å	$\beta=105.46$ (2)°
$c=10.229$ (2) Å	$\gamma=76.43$ (2)°
$V=1689.1$ (6) Å^3	$Z=2$
$D_M=1.310$ g cm^{-3}	$D_X=1.305$ g cm^{-3}
$\mu=1.24$ mm^{-1} (for Mo $K\alpha$ radiation)	$F(000)=688$

[a] The numbers in parentheses, here and elsewhere in this paper, are the e.s.d.'s in the last significant digits.

Intensity data of 4404 independent reflections within a range of $2\theta<45°$ were collected by an ω-2θ scanning technique. Of these, 3434 reflections with $F_o>2.0\sigma(F_o)$ were used for the structure analysis. The intensity data were corrected for Lorentz and polarization effects, but not for absorption or extinction. The statistical distribution of the normalized structure factors favoured the centrosymmetric space group, which was confirmed by the convergence of the structure at a later stage of the refinement.

Structure Determination and Refinement

The Br-atom position was easily deduced from a Patterson synthesis, and the remaining non-H atoms of ICPA molecule were located in a subsequent Fourier map. Refinement was carried out by the block-diagonal least-squares procedures, in which initially equal weights and later Cruickshank's weighting scheme were adopted.[2] After several cycles of refinements with isotropic and then anisotropic thermal parameters, the H atoms were located in difference Fourier maps, in which also eight peaks with three times the height of these H atoms were found between ICPA molecules. These peaks were interpreted as disordered acetone atoms with an occupancy factor of 0.5. After the removal of the five strong reflections affected by secondary extinction and of one reflection with a strong imbalance of the background intensities, refinement was terminated when all shift/e.s.d. for non-H atoms of ICPA became less than 0.3. The final difference Fourier synthesis showed two implausible peaks of *ca.* 0.6 eÅ^{-3} in the vicinity of the Br atom and eight peaks of 0.3—0.5 eÅ^{-3} distributed at random in the vicinities of the acetone atoms. This suggested that the model of the disordered acetone was yet ambiguous, but no attempt was made to clarify the disorder. Thus, the molecular dimensions of the acetone were omitted from the later table and discussion. The final conventional R index was 0.050 for 3428 measurable reflections. The

Table 2. Fractional atomic coordinates and thermal parameters

(a) Non-H atoms of ICPA molecule.
The coordinate values have been multiplied by 10^4. The B_{eq}'s are the equivalent values of the anisotropic thermal parameters, following the definition given by Hamilton.[8]

Atom	x	y	z	B_{eq}/Å^2
Br	5802.4(6)	6295.0(4)	6888.7(5)	5.36(1)
C(1)	4436(4)	8939(3)	-2034(5)	4.0(2)
C(2)	4095(5)	9078(4)	-3438(6)	4.7(2)
C(3)	4930(6)	9055(4)	-4172(5)	4.9(2)
C(3a)	6198(5)	8870(3)	-3549(5)	3.8(1)
C(4)	7183(5)	8834(3)	-4131(5)	4.4(2)
C(5)	8358(5)	8617(3)	-3384(5)	4.2(2)
C(6)	8665(4)	8415(3)	-1995(5)	3.7(1)
C(6a)	7735(4)	8458(3)	-1381(4)	3.0(1)
C(6b)	7739(4)	8235(3)	48(4)	2.8(1)
C(6c)	7903(4)	7184(3)	140(4)	2.6(1)
C(6d)	9014(4)	6550(3)	935(4)	2.9(1)
C(7)	10235(4)	6433(3)	947(5)	3.9(1)
C(8)	11078(5)	5739(4)	1673(6)	5.1(2)
C(9)	10709(5)	5159(4)	2348(6)	5.4(2)
C(10)	9504(5)	5262(3)	2354(6)	4.4(2)
C(10a)	8653(4)	5964(3)	1638(4)	3.0(1)
C(11)	7261(4)	6175(3)	1458(4)	2.7(1)
C(11a)	6899(4)	7082(3)	757(4)	2.5(1)
C(12)	6006(4)	7829(3)	698(4)	2.5(1)
C(12a)	6340(4)	8580(3)	83(4)	2.8(1)
C(12b)	5660(4)	8753(3)	-1386(4)	3.0(1)
C(12c)	6521(4)	8707(3)	-2146(4)	3.0(1)
N(1)	8640(3)	8606(2)	1094(4)	3.1(1)
C(13)	8616(5)	9572(3)	951(5)	4.1(2)
C(14)	9346(6)	9860(4)	2308(6)	5.4(2)
C(15)	9373(6)	9178(5)	3301(6)	6.1(2)
C(16)	8614(5)	8531(4)	2504(5)	4.0(2)
C(17)	6762(4)	5477(3)	488(4)	2.9(1)
N(2)	6390(4)	4945(3)	-265(4)	4.4(1)
C(18)	6871(4)	6191(3)	2783(4)	2.8(1)
C(19)	5922(4)	5814(3)	2870(4)	3.5(1)
C(20)	5589(5)	5861(4)	4081(5)	4.2(2)
C(21)	6216(4)	6261(3)	5209(4)	3.4(1)
C(22)	7166(4)	6640(3)	5150(4)	316(1)
C(23)	7487(4)	6610(3)	3945(5)	3.4(1)
C(24)	4831(4)	7962(3)	1060(4)	2.7(1)
C(25)	4151(4)	7299(3)	712(6)	4.2(2)
C(26)	3021(5)	7420(4)	965(7)	5.5(2)
C(27)	2541(5)	8215(4)	1585(6)	5.1(2)
C(28)	3193(5)	8884(3)	1948(6)	4.4(2)
C(29)	4330(4)	8764(3)	1687(5)	3.5(1)

(b) H atoms of ICPA molecule.
The H atoms are labelled in terms of the C atom to which they are are attached. The coordinate values have been multiplied by 10^3.

Atom	x	y	z	B/Å^2
H(1)	384(4)	895(3)	-152(4)	4(1)
H(2)	322(4)	918(3)	-387(5)	4(1)
H(3)	466(4)	921(3)	-504(5)	5(1)
H(4)	704(4)	897(3)	-500(5)	5(1)
H(5)	906(4)	860(3)	-380(4)	4(1)
H(6)	949(4)	825(3)	-153(4)	3(1)
H(6c)	774(3)	695(2)	-77(3)	2(1)
H(7)	1048(4)	683(3)	45(4)	4(1)
H(8)	1187(4)	571(3)	167(5)	5(1)
H(9)	1125(5)	475(4)	280(5)	6(1)
H(10)	924(5)	489(3)	280(5)	5(1)
H(12a)	622(3)	916(3)	66(4)	3(1)
H(13)1	772(4)	993(3)	76(5)	4(1)
H(13)2	898(4)	964(3)	21(4)	4(1)
H(14)1	1015(5)	986(3)	232(5)	5(1)
H(14)2	902(6)	1048(4)	261(6)	8(2)
H(15)1	1024(5)	884(4)	369(6)	7(1)
H(15)2	909(6)	939(4)	411(6)	8(2)
H(16)1	776(5)	878(3)	264(5)	6(1)
H(16)2	882(5)	790(4)	285(6)	7(1)
H(19)	554(5)	550(4)	213(5)	6(1)
H(20)	494(4)	563(3)	414(5)	5(1)
H(22)	754(4)	692(3)	587(4)	4(1)
H(23)	816(4)	693(3)	387(5)	5(1)
H(25)	445(4)	681(3)	20(5)	4(1)
H(26)	255(4)	691(3)	67(4)	4(1)
H(27)	171(5)	830(4)	173(5)	6(1)
H(28)	283(5)	953(4)	242(6)	8(1)
H(29)	479(4)	918(3)	199(5)	5(1)

(c) Disordered acetone atoms.
The occupancy factor was fixed at 0.5. The coordinate values have been multiplied by 10^3.

	x	y	z	B/Å^2
O	775(1)	313(1)	266(1)	12(1)
C(30)	841(2)	289(1)	411(2)	9(1)
C(31)	800(2)	350(2)	499(3)	14(1)
C(32)	958(2)	300(1)	448(2)	10(1)
O'	760(1)	293(1)	524(1)	11(1)
C(30)'	804(2)	258(2)	403(2)	12(1)
C(31)'	860(1)	191(1)	387(2)	8(1)
C(32)'	857(2)	333(2)	380(2)	13(1)

atomic scattering factors for Br, O, N, and C_{cov}, with correction factors for anomalous dispersion, were taken from International Tables for X-ray Crystallography.[3] Those for H were adopted from the table of Stewart *et al.*[4] All the calculations were carried out on a FACOM M-200 computer in the Computer Center of Kyushu University by the use of locally modified versions of the UNICS-III program system.[5,6] Figures. 1 and 3 were drawn by the use of the ORTEP program.[7] The final atomic parameters are listed in Table. 2, together with their e.s.d.'s. Lists of the structure factors and anisotropic thermal parameters have been deposited as Document No. 8341 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.

Results and Discussion

The molecular structure of ICPA was confirmed by

TABLE 3. BOND ANGLES

Bond angle	$\theta/°$	Bond angle	$\theta/°$	Bond angle	$\theta/°$
C(12b)-C(1)-C(2)	118.3(5)	C(8)-C(9)-C(10)	121.6(5)	C(6b)-N(1)-C(13)	114.7(3)
C(1)-C(2)-C(3)	122.7(5)	C(9)-C(10)-C(10a)	118.2(6)	C(6b)-N(1)-C(16)	116.5(4)
C(2)-C(3)-C(3a)	121.0(5)	C(10)-C(10a)-C(6d)	120.8(5)	C(13)-N(1)-C(16)	105.7(4)
C(3)-C(3a)-C(12c)	115.3(5)	C(10)-C(10a)-C(11)	126.8(5)	N(1)-C(13)-C(14)	104.4(4)
C(3)-C(3a)-C(4)	129.0(5)	C(6d)-C(10a)-C(11)	112.4(4)	C(13)-C(14)-C(15)	106.3(5)
C(12c)-C(3a)-C(4)	115.7(4)	C(10a)-C(11)-C(11a)	100.2(4)	C(14)-C(15)-C(16)	106.0(5)
C(3a)-C(4)-C(5)	121.1(5)	C(10a)-C(11)-C(17)	107.7(4)	C(15)-C(16)-N(1)	104.3(6)
C(4)-C(5)-C(6)	122.4(6)	C(10a)-C(11)-C(18)	114.2(3)	C(11)-C(17)-N(2)	179.1(6)
C(5)-C(6)-C(6a)	118.6(4)	C(11a)-C(11)-C(17)	109.1(3)	C(11)-C(18)-C(19)	122.7(4)
C(6)-C(6a)-C(12c)	119.0(4)	C(11a)-C(11)-C(18)	115.5(4)	C(11)-C(18)-C(23)	119.0(5)
C(6)-C(6a)-C(6b)	132.1(4)	C(17)-C(11)-C(18)	109.6(4)	C(19)-C(18)-C(23)	118.4(4)
C(12c)-C(6a)-C(6b)	108.9(4)	C(11)-C(11a)-C(6c)	109.8(4)	C(18)-C(19)-C(20)	120.6(4)
C(6a)-C(6b)-C(6c)	109.9(3)	C(11)-C(11a)-C(12)	136.0(5)	C(19)-C(20)-C(21)	120.1(6)
C(6a)-C(6b)-(12a)	103.2(3)	C(6c)-C(11a)-C(12)	113.6(4)	C(20)-C(21)-C(22)	120.5(5)
C(6a)-C(6b)-N(1)	112.2(4)	C(11a)-C(12)-C(12a)	108.9(4)	C(21)-C(22)-C(23)	119.7(4)
C(12a)-C(6b)-C(6c)	100.8(4)	C(11a)-C(12)-C(24)	129.4(5)	C(22)-C(28)-C(18)	120.8(5)
C(12a)-C(6b)-N(1)	117.1(4)	C(12a)-C(12)-C(24)	121.6(4)	C(20)-C(21)-Br	120.5(4)
C(6c)-C(6b)-N(1)	112.7(3)	C(12)-C(12a)-C(6b)	106.5(3)	C(22)-C(21)-Br	119.0(3)
C(6b)-C(6c)-C(11a)	104.9(4)	C(12)-C(12a)-C(12b)	114.5(4)	C(12)-C(24)-C(25)	120.1(4)
C(6b)-C(6c)-C(6d)	126.1(4)	C(6b)-C(12a)-C(12b)	104.5(4)	C(12)-C(24)-C(29)	122.2(5)
C(11a)-C(6c)-C(6d)	103.2(4)	C(12a)-C(12b)-C(12c)	108.6(4)	C(25)-C(24)-C(29)	117.6(5)
C(6c)-C(6d)-C(10a)	109.7(4)	C(12a)-C(12b)-C(1)	132.4(5)	C(24)-C(25)-C(26)	121.7(5)
C(6c)-C(6d)-C(7)	130.1(5)	C(1)-C(12b)-C(12c)	119.0(5)	C(25)-C(26)-C(27)	119.9(6)
C(10a)-C(6d)-C(7)	120.0(4)	C(3a)-C(12c)-C(6a)	123.2(5)	C(26)-C(27)-C(28)	119.9(6)
C(6d)-C(7)-C(8)	119.0(5)	C(3a)-C(12c)-C(12b)	123.6(4)	C(27)-C(28)-C(29)	120.2(5)
C(7)-C(8)-C(9)	120.6(5)	C(6a)-C(12c)-C(12b)	113.2(4)	C(28)-C(29)-C(24)	120.6(5)

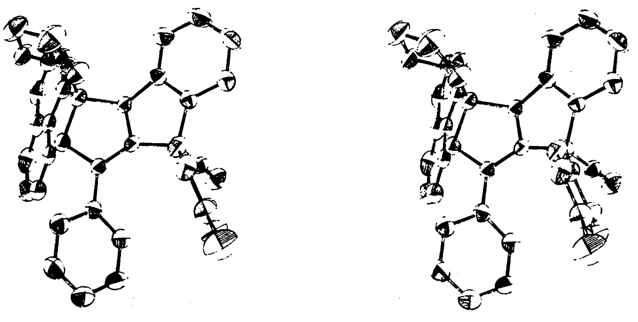

Fig. 1. Stereoscopic view of the molecular structure of ICPA. The thermal-motion ellipsoids are scaled to enclose 50% probability. The H atoms have been omitted for clarity, and likewise in the following figures.

this X-ray structural study. A stereoscopic view of this molecular structure is shown in Fig. 1. The bond distances(l) are shown schematically in Fig. 2, together with the atomic-nomenclature scheme. The bond angles(θ) are listed in Table 3.

The naphthalene ring [A] deviates slightly from planarity, the maximum deviation being 0.04 Å, as shown in Table 4. C(6b) is shifted by 0.17 Å from this plane, whereas C(12a) is displaced 0.11 Å in the opposite direction, so that the acenaphthene ring has a somewhat twisted conformation. The distance of the C(6b)–C(12a) bond, which is shared between the acenaphthene and the central cyclopentane ring [C(6b), C(6c), C(11a), C(12), and C(12a)], is unusually long (1.596(6) Å). This may result from the additional strain induced on the bond by the fusion of these rings. A similar phenomenon has been observed in a series of fused acenaphthylenes, $C_{14}H_{10}$, $C_{18}H_{12}$, $C_{22}H_{14}$, and $C_{26}H_{14}N_2$.[9–12] The central cyclopentane ring is slightly puckered in an envelope-like conformation; the maximum torsion angle is 21.8(4)° about the C(6b)–C(6c) bond, and C(6b) is shifted by 0.38 Å from the plane through the other four atoms. The B ring [C(6d) through C(10a)] is planar within limits of the experimental error. C(6c) and C(11a) were found to lie almost equidistant from the plane on different sides, and so the indane ring has a

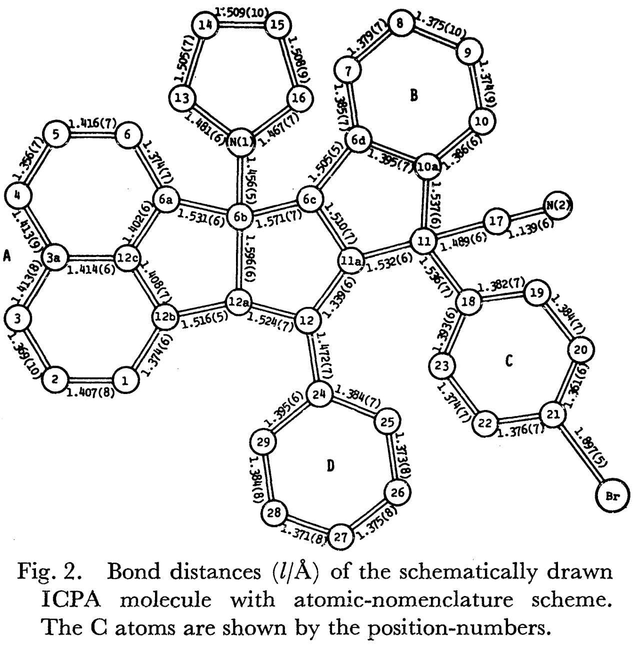

Fig. 2. Bond distances (l/Å) of the schematically drawn ICPA molecule with atomic-nomenclature scheme. The C atoms are shown by the position-numbers.

Table 4. Least-squares planes and torsion angles

(a) Deviations (l/Å) from least-squares planes.
Atoms with an asterisk are not included in the plane calculation.

ring A		ring B		ring C		ring D	
C(1)	0.017	C(6d)	−0.000	C(18)	−0.002	C(24)	−0.001
C(2)	−0.033	C(7)	−0.005	C(19)	−0.006	C(25)	0.002
C(3)	−0.028	C(8)	0.008	C(20)	0.009	C(26)	−0.001
C(3a)	0.002	C(9)	−0.006	C(21)	−0.005	C(27)	−0.001
C(4)	0.035	C(10)	0.001	C(22)	−0.003	C(28)	0.002
C(5)	0.020	C(10a)	0.002	C(23)	0.006	C(29)	−0.001
C(6)	−0.030	C(6c)*	−0.137	C(11)*	0.011	C(12)*	−0.079
C(6a)	0.039	C(11)*	−0.052	Br*	−0.042		
C(12b)	0.042	C(11a)*	0.174				
C(12c)	0.014						
C(6b)*	−0.166						
C(12a)*	0.109						

(b) Selected torsion angles (θ/°)

Central cyclopentane ring

C(6b)-C(6c)-C(11a)-C(12)	17.1(5)
C(6c)-C(11a)-C(12)-C(12a)	−3.4(5)
C(11a)-C(12)-C(12a)-C(6b)	−11.6(5)
C(12)-C(12a)-C(6b)-C(6c)	20.5(4)
C(12a)-C(6b)-C(6c)-C(11a)	−21.8(4)

Around the C(6b)-N(1) bond

C(6a)-C(6b)-N(1)-C(13)	48.4(5)
C(6c)-C(6b)-N(1)-C(13)	173.1(4)
C(12a)-C(6b)-N(1)-C(13)	−70.6(5)

Pyrrolidine ring

N(1)-C(13)-C(14)-C(15)	−19.6(6)
C(13)-C(14)-C(15)-C(16)	−2.2(7)
C(14)-C(15)-C(16)-N(1)	23.4(6)
C(15)-C(16)-N(1)-C(13)	−36.3(5)
C(16)-N(1)-C(13)-C(14)	35.0(5)

somewhat twisted conformation. The plane of the B ring makes an angle of 42.0° with the naphthalene ring. Thus, the body of the molecule has an uncomfortable chair form.

The pyrrolidine ring is in the normal envelope conformation, with N(1) out of the plane of the other four atoms. The torsion angles about the C(6b)–N(1) bond are close to 50, 170, and 290°, so that the lone pair of electrons of N(1) is *cis* to C(12a). The D ring [C(24) through C(29)] is planar within the limits of experimental error, and this plane is tuned from the plane through the four atoms [C(11a), C(12), C(12a), and C(24)] by an angle of 42.1° away from the naphthalene moiety. The bromophenyl group faces the D ring at an angle of *ca.* 60°. The bromophenyl group is *cis* to the pyrrolidine, so that the close contact between the two groups is 2.26(9) Å of the H(16)2···H(23) distance.

The C–H bond distances are in the range from 0.84 to 1.09 Å, with an average of 0.96(6) Å, and the bond angles involving the H atoms are reasonable. These bond distances and angles have been omitted in Table 3, since the H atoms were unlikely to play a role except in crystal packing.

The crystal structure projected along the c axis is shown in Fig. 3. There is a channel parallel to the c axis extending throughout the entire crystal. Acetone molecule is contained in this channel, without close contact with the main molecule. This explains the easy loss of acetone from the crystal.

The structure of the minor product was presumed to be stereoisomer of the present compound, with a different configuration only at the C(11) atom.[1)]

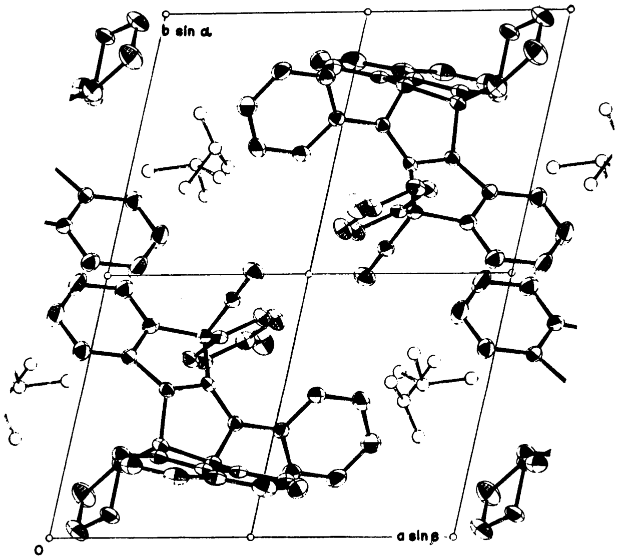

Fig. 3. The crystal structure projected along the c axis. The thermal-motion elliposids are scaled to enclose 30% probability, and acetone atoms are shown as open circles of arbitrary size.

The authors are grateful to Professor Shigeo Kida of the Faculty of Science, Kyushu University, for allowing us to use the automated diffractometer, and to Asst. Professor Shigeaki Kawano of the College of General Eduction of this University for his advice with regard to the computation process.

References

1) O. Tsuge, S. Okita, M. Noguchi, and S. Kanemasa, *Chem. Lett.*, **1982**, 993.

2) D. W. J. Cruickshank, "Computing Methods in Crystallography," ed by J. S. Rollett, Pergamon Press, Oxford (1965), p. 112.

3) "International Tables for X-ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, p. 72.

4) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

5) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku* (in Japanese), **55**, 69 (1979).

6) S. Kawano, *Rep. Comp. Cent. Kyushu Univ.* (in Japanese), **16**, 113 (1983).

7) C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee (1965).

8) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).

9) A. C. Hazell, *Acta Crystallogr., Sect. B*, **32**, 2010 (1976).

10) A. C. Hazell and R. G. Hazell, *Acta Crystallogr., Sect. B*, **33**, 360 (1977).

11) A. C. Hazell and Å. Weigelt, *Acta Crystallogr., Sect. B*, **32**, 306 (1976).

12) C. Courseille, B. Busetta, M. Hospital, and A. Castellan, *Cryst. Struct. Commun.*, **1**, 337 (1972).