ELIEL, E. L. & KNOEBER, M. C. (1968). *J. Am. Chem. Soc.* **90**, 3444–3458.

GORRICHON, J. P., GASET, A. & DELMAS, M. (1979). *Synthesis*, pp. 219–220.

KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.

KOK, D. DE & ROMERS, C. (1970). *Recl Trav. Chim. Pays-Bas*, **89**, 313.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. de York, Angleterre, et Louvain-la-Neuve, Belgique.

MOTHERWELL, S. & CLEGG, B. (1978). *PLUTO.* Programme pour le dessin de structures cristallines et moléculaires. Univ. de Cambridge, Angleterre.

NADER, F. W. (1975). *Tetrahedron Lett.* pp. 1207–1210, 1591–1594.

SHELDRICK, G. M. (1976). *SHELX* 76. Programme pour la détermination de structures cristallines. Univ. de Cambridge, Angleterre.

WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*, pp. 101–102. Cambridge Univ. Press.

Acta Cryst. (1981). B**37**, 625–629

Synthesis, Crystal Structure and Conformation of the Cyclic Dipeptide *cyclo*(-L-Seryl-L-seryl-)

BY GIOVANNA GASPARRI FAVA AND MARISA FERRARI BELICCHI

Centro di Studio per la Strutturistica Diffrattometrica del CNR, Istituti di Chimica Generale e Strutturistica Chimica dell'Università di Parma, Italy

AND ROSANGELA MARCHELLI AND ARNALDO DOSSENA

Istituto di Chimica Organica, Università di Parma, 43100 *Parma, Italy*

(*Received* 26 *March* 1980; *accepted* 26 *November* 1980)

Abstract

The synthesis, spectral data and X-ray structure determination of the cyclic dipeptide *cyclo*(-L-Ser-L-Ser-), $C_6H_{10}N_2O_4$, are reported. The compound was obtained by intramolecular aminolysis of two serine residues bridged *via* esteric bonds by a hydrocarbon chain. IR, CD and ^{1}H NMR spectra are discussed in order to determine the salient features of the structure in solution. Crystals are orthorhombic, space group $P2_12_12_1$, with cell dimensions $a = 11{\cdot}096\,(2)$, $b = 7{\cdot}787\,(1)$, $c = 8{\cdot}538\,(1)$ Å; $R = 0{\cdot}053$ for 784 observed reflections. The diketopiperazine ring (DKP) is nearly planar. Intermolecular hydrogen bonds connect the DKP rings in spirals parallel to the [001] axis.

Introduction

Cyclic peptides are suitable models for conformational analysis, being more constrained than their corresponding linear analogs (Deber, Madison & Blout, 1976). The simplest cyclic peptides, the diketopiperazines, have been extensively studied by X-rays in the solid state (Lin & Webb, 1973; Benedetti, Marsh & Goodman, 1976; Cotrait, Ptak, Busetta & Hetz, 1976; Ramani, Venkatesan & Marsh, 1978), and by ^{1}H NMR in solution (Hruby, 1974), since they combine biological importance with structural simplicity.

In connection with our previous work on natural products containing this structural system (echinulin and neoechinulins; Marchelli, Dossena, Pochini & Dradi, 1977) and our general interest in structure modifications of amino acids and oligopeptides (Dossena, Rizzo, Marchelli, Casnati & Luisi, 1976), we report here the synthesis, spectral data and X-ray structure determination of the cyclic dipeptide *cyclo*(-L-Ser-L-Ser-). Although this compound appeared in the literature many years ago (Fisher & Jacobs, 1906), its structure determination has not been reported. Since serine is present in the active site of proteolytic enzymes such as α-chymotrypsin (Blow, 1976), we thought it interesting to investigate the conformation of this diketopiperazine, both in the solid state and in solution.

0567-7408/81/030625-05$01.00

Experimental

Synthesis and spectral data

cyclo(-L-Ser-L-Ser-) was prepared by cyclization of pentamethylene di(Z-L-serinate), prepared by a method described previously (Bocchi, Casnati, Dossena & Marchelli, 1979), by hydrogenation in the presence of 5% Pd/C in methanol for 1·30 h. The catalyst was removed by filtration and the reaction mixture was evaporated to a small bulk under vacuum at 313 K. The product was crystallized from water. Yield ~95%; m.p. (decomposition) = 503 K; $M^+ + 1 = 175$; elemental analysis: calculated for $C_6H_{10}N_2O_4$: C 41·38, H 5·79, N 16·09%; found C 41·12, H 5·80, N 16·13%; $[\alpha]_D^{298\,K}$ = −67·09 (2·0% in H_2O), IR (KBr) 3230, 1675, 1460 cm^{-1}; ^1H NMR [$(CD_3)_2SO$ + CF_3COOD] (δ) 8·10 (~2H, broad *s*), 3·80–3·95 (6H, *m*) p.p.m.; CD (H_2O) 207 nm.

Physical measurements

The IR spectra (in KBr pellets) were recorded on a Perkin–Elmer 457 spectrophotometer. The instrument used for CD measurements was a Jasco spectropolarimeter. The ^1H NMR spectra were recorded on a Varian X-L 100 MHz spectrometer, using Me_4Si as internal standard. Mass spectra were recorded on a Varian Mat CH-5 mass spectrometer. $[\alpha]_D^{298\,K}$ were obtained from a Perkin–Elmer 141 polarimeter.

Crystal data

cyclo(-L-Ser-L-Ser-) was crystallized from water as thin colourless needle-shaped crystals suitable for the X-ray analysis. The space group was determined from Weissenberg photographs; the cell parameters and intensities were measured at room temperature on an automated Siemens AED single-crystal diffractometer (Cu $K\alpha$ radiation, $\bar{\lambda}$ = 1·54178 Å) by the ω–2θ scanning technique. Cell dimensions were refined by least-squares fits to the (θ,χ,φ) values for 20 reflections measured on the diffractometer.

$C_6H_{10}N_2O_4$, M_r = 174·16, orthorhombic, a = 11·096 (2), b = 7·787 (1), c = 8·538 (1) Å; U = 737·7 Å^3, D_c = 1·57 Mg m^{-3}, Z = 4; $F(000)$ = 368; μ(Cu $K\alpha$) = 1·154 mm^{-1}. Space group $P2_12_12_1$ (from systematic absences). Crystal dimensions: 0·49 × 0·07 × 0·07 mm.

Data collection

All the reflections with $2\theta < 140°$ were collected; in this way 842 independent reflections were measured, of which 784 with $I > 2\sigma(I)$ were considered as observed and used in the subsequent analysis. Corrections for Lorentz and polarization factors were made, but not for absorption as the sample was sufficiently small. The first absolute scaling and the overall isotropic temperature factor were obtained by Wilson's (1942) method.

Structure analysis

The structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971; Declercq, Germain, Main & Woolfson, 1973). Use of *MULTAN* for 160 reflections with $|E| > 1·3$ led to a satisfactory set of starting reflections and 64 combinations of starting phases. After phase expansion, the E map, calculated for the solution with the third-largest absolute figure of merit, 1·280, and the largest combined figure of merit, 2·998, contained peaks at stereochemically reasonable positions for all the atoms of the cyclic dipeptide.

The structure was refined by full-matrix least squares, at first with isotropic then with anisotropic thermal parameters. All the H atoms have been directly located from a final difference map. The final conventional R index was 0·053 (observed reflections only).

Table 1. *Fractional atomic coordinates* (×10^4; *for* H ×10^3) *and equivalent isotropic thermal parameters* (Å^2)

	x	y	z	B_{eq}*		x	y	z
O(1)	4489 (3)	−956 (4)	2501 (4)	2·59	H(1)	349 (5)	181 (8)	262 (8)
O(2)	1171 (3)	1649 (5)	4538 (4)	2·72	H(2)	385 (5)	368 (8)	471 (7)
O(3)	3314 (3)	2736 (4)	7567 (4)	2·53	H(3)	417 (5)	−15 (8)	748 (8)
O(4)	2498 (3)	−2512 (5)	5520 (4)	2·88	H(4)	529 (5)	−101 (8)	534 (7)
N(1)	3616 (4)	1400 (5)	3528 (4)	1·84	H(51)	193 (6)	399 (9)	355 (8)
N(2)	3994 (4)	248 (5)	6545 (4)	1·98	H(52)	168 (6)	393 (9)	562 (8)
C(1)	4150 (4)	−118 (6)	3651 (5)	2·72	H(61)	417 (6)	−323 (8)	655 (8)
C(2)	3291 (4)	2545 (6)	4803 (5)	2·53	H(62)	410 (6)	−341 (9)	444 (8)
C(3)	3538 (4)	1817 (6)	6419 (5)	2·88	H(7)	224 (6)	−250 (10)	458 (9)
C(4)	4377 (4)	−866 (6)	5260 (5)	1·84	H(8)	104 (6)	126 (9)	545 (8)
C(5)	1963 (4)	3089 (6)	4665 (6)	1·98				
C(6)	3773 (5)	−2640 (6)	5417 (6)	1·73				

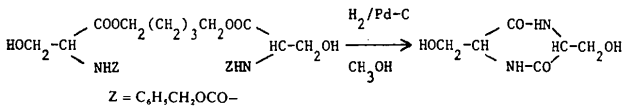
* Defined according to Hamilton (1959).

Atomic scattering factors used throughout the calculations were taken from Cromer & Mann (1968) for non-hydrogen atoms and from Stewart, Davidson & Simpson (1965) for H atoms. Positional parameters with their estimated standard deviations are given in Table 1.†

Results and discussion

Synthesis

In connection with our general interest in the syntheses and conformations of amino acid derivatives, we synthesized, among others, pentamethylene di(Z-L-serinate), which, upon deprotection by hydrogenation with Pd/C, afforded the cyclic dipeptide *cyclo*(-L-Ser-L-Ser-). As expected, the serine OH catalysed the intramolecular aminolysis of the ester.



(I) (II)

The yield in isolated product is quantitative (>95%) after 1·30 h (overall yield from L-serine ≥ 80%); the optical purity is 98%.

Spectral data

The IR spectrum (in KBr) of *cyclo*(-L-Ser-L-Ser-) shows a broad absorption at 3230 cm^{-1} (bonded secondary amide NH and bonded OH stretching) and the amide I peak at 1675 cm^{-1}. Being a *cis* peptide, it shows no absorption in the 1550 cm^{-1} region, while the amide II band occurs at 1460 cm^{-1}.

The CD spectrum reveals a negative band at 207 nm, probably due to the exciton split π–π^* transition of the peptide, as seen in the α helix and totally lost in the random coil. This seems to suggest that the π–π^* transition of the peptide chromophore can be displayed if a certain molecular rigidity (as existing in the DKP ring), a particular orientation of perturbing atoms and the required disposition of the two identical chromophores (in which case the DKP ring might be non-planar) are realized. This is in agreement with the conclusions drawn by Balasubramanian & Wetlaufer (1967) for *cyclo*(-L-Ala-L-Ser-), *cyclo*(-L-Ala-L-Ala-) and *cyclo*(-L-Ala-L-Phe-) on the basis of combined CD and ORD results.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35747 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The ^1H NMR spectrum [in $(CD_3)_2SO$ and traces of CF_3COOD] does not provide a clear picture of the behaviour of *cyclo*(-L-Ser-L-Ser-) in solution. A broad complex absorption is present at δ3·8–3·9 p.p.m. In general, in the absence of aromatic side chains, the lessened importance of intramolecular interactions is expected to make the DKP ring conformations quite close in energy. However, the eventual magnetic non-equivalence in Me_2SO is perturbed in the presence of traces of trifluoroacetic acid, added for solubility reasons.

Crystal structure

Bond lengths and angles are listed in Table 2. In the present compound only small differences are observed in the geometry of the DKP ring as compared with other cyclic dipeptides, *e.g.* *cyclo*(-L-Ser-L-His-) (Cotrait & Ptak, 1978), *cyclo*(-L-Thr-L-His-) (Cotrait, Ptak, Busetta & Hetz, 1976), *cyclo*(-Gly-L-Tyr-) and *cyclo*(-L-Ser-L-Tyr-) (Lin & Webb, 1973).

The conformation is defined by two sets of φ, ψ and ω angles for the DKP ring and by χ_1^1 and χ_2^1 angles for the side chains. The DKP ring is nearly planar (equation in orthogonal Å coordinates: $0{\cdot}9105X + 0{\cdot}4135Y - 0{\cdot}0032Z = 4{\cdot}1228$); deviations are C(2)^a 0·008, N(1) −0·029, C(1) 0·022, C(4)^a 0·006, N(2) −0·026, C(3) 0·020 Å. The puckering amplitudes (Q = 0·047, q_2 = 0·05, $|q_3|$ = 0·01 Å, θ = 95·7, φ = 223·3°) (Cremer & Pople, 1975) describe a rather flattened twist-boat conformation. Torsional angles

Table 2. *Bond distances* (Å) *and angles* (°)

C(1)–N(1)	1·326 (6)	O(4)–C(6)	1·421 (7)
N(1)–C(2)	1·453 (6)	N(1)–H(1)	0·85 (7)
C(2)–C(3)	1·517 (6)	C(2)–H(2)	1·08 (6)
C(3)–N(2)	1·327 (6)	C(5)–H(51)	1·18 (7)
N(2)–C(4)	1·462 (6)	C(5)–H(52)	1·09 (7)
C(1)–C(4)	1·513 (6)	O(2)–H(8)	0·85 (7)
O(1)–C(1)	1·236 (6)	N(2)–H(3)	0·88 (7)
C(2)–C(5)	1·538 (6)	C(4)–H(4)	1·03 (6)
O(2)–C(5)	1·429 (6)	C(6)–H(61)	1·16 (7)
O(3)–C(3)	1·239 (6)	C(6)–H(62)	1·09 (7)
C(4)–C(6)	1·541 (7)	O(4)–H(7)	0·85 (8)

O(1)–C(1)–N(1)	122·9 (0·4)	N(2)–C(4)–H(4)	107·9 (3·3)
O(1)–C(1)–C(4)	117·8 (0·4)	N(2)–C(4)–C(6)	109·9 (0·4)
N(1)–C(1)–C(4)	119·3 (0·4)	C(1)–C(4)–H(4)	105·4 (3·3)
C(1)–N(1)–H(1)	118·8 (4·3)	C(1)–C(4)–C(6)	110·6 (0·4)
C(2)–N(1)–H(1)	114·3 (4·3)	C(6)–C(4)–H(4)	109·0 (3·3)
C(1)–N(1)–C(2)	126·8 (0·4)	O(2)–C(5)–C(2)	112·3 (0·4)
N(1)–C(2)–H(2)	107·6 (3·2)	C(2)–C(5)–H(52)	112·6 (3·6)
N(1)–C(2)–C(5)	110·5 (0·4)	C(2)–C(5)–H(51)	104·8 (3·3)
N(1)–C(2)–C(3)	114·0 (0·4)	O(2)–C(5)–H(51)	112·7 (3·3)
C(5)–C(2)–H(2)	108·7 (3·2)	O(2)–C(5)–H(52)	110·6 (3·6)
C(3)–C(2)–H(2)	105·6 (3·2)	H(51)–C(5)–H(52)	103·6 (4·8)
C(3)–C(2)–C(5)	110·2 (0·4)	O(4)–C(6)–C(4)	112·1 (0·4)
N(2)–C(3)–C(2)	119·1 (0·4)	C(4)–C(6)–H(61)	105·1 (3·4)
O(3)–C(3)–C(2)	117·9 (0·4)	C(4)–C(6)–H(62)	106·4 (3·5)
O(3)–C(3)–N(2)	123·0 (0·4)	O(4)–C(6)–H(61)	110·8 (3·4)
C(3)–N(2)–C(4)	126·6 (0·4)	O(4)–C(6)–H(62)	114·6 (3·5)
C(3)–N(2)–H(3)	118·8 (4·2)	H(61)–C(6)–H(62)	107·3 (4·9)
C(4)–N(2)–H(3)	114·2 (4·2)	C(5)–O(2)–H(8)	108·7 (4·8)
N(2)–C(4)–C(1)	113·9 (0·4)	C(6)–O(4)–H(7)	106·0 (5·1)

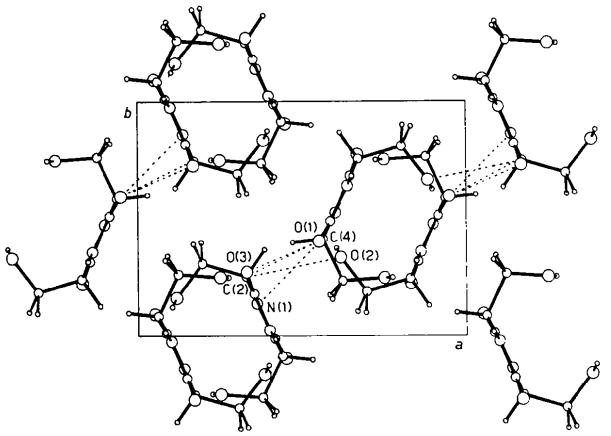


Fig. 1. Projection of the structure on the (001) plane.

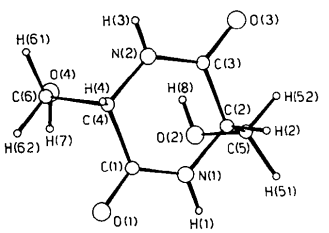


Fig. 2. Projection of the molecule on the (100) plane

Table 3. *Contacts* <3·5 Å

Symmetry code

(I)	$\frac{1}{2}-x$, $\bar{y}$, $z-\frac{1}{2}$	(III)	$x-\frac{1}{2}$, $\frac{1}{2}-y$, $1-z$
(II)	$1-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$	(IV)	$1-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$

O(1)···O(2^{I})	2·688 (5) Å	O(2)···C(2^{III})	3·305 (6) Å
O(4)···O(3^{I})	2·683 (5)	O(2)···C(3^{III})	3·260 (6)
N(1)···O(4^{I})	2·979 (5)	O(3)···C(4^{IV})	3·345 (6)
O(2)···N(2^{I})	2·957 (5)	O(1)···O(3^{I})	3·406 (5)
O(1)···N(1^{II})	3·071 (6)	C(6)···O(3^{I})	3·360 (6)
O(1)···C(2^{II})	3·362 (6)	O(1)···C(5^{I})	3·349 (6)

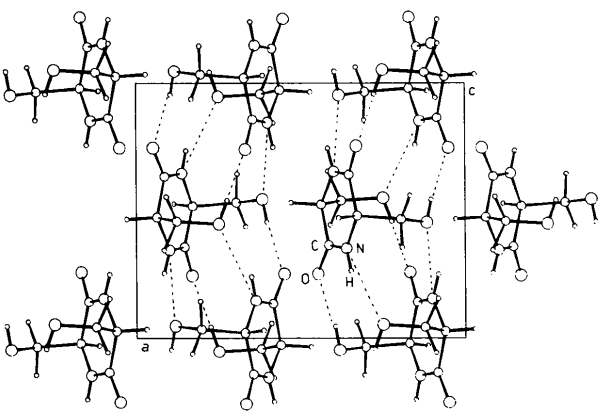


Fig. 3. Projection of the structure on the (010) plane. Dashed lines indicate hydrogen bonds.

[using the convention of the IUPAC–IUB Commission on Biochemical Nomenclature (1970)] take the following values: $\varphi_1 = -4{\cdot}0$ (6), $\psi_1 = -1{\cdot}0$ (6), $\omega_1 = 4{\cdot}5$ (7), $\varphi_2 = -3{\cdot}2$ (6), $\psi_2 = -1{\cdot}7$ (6), $\omega_2 = 5{\cdot}4$ (7)° [e.s.d.'s following Stanford & Waser (1972)].

The L-Ser side chains are folded above the DKP ring, with the substituents on the C^{α} atoms in the quasi-axial position directed towards each other across the ring (Figs. 1, 2). The torsion angles χ_1^1 and χ_2^1 are respectively 53·2 (5) and 54·6 (5)°. Such a folded conformation was also found in *cyclo*(-L-Ser-L-His-) (Cotrait & Ptak, 1978) with $\chi_1^1 = 69{\cdot}8°$ and in *cyclo*(-L-Thr-L-His-) (Cotrait, Ptak, Busetta & Hetz, 1976) with $\chi_1^1 = 69{\cdot}5°$. The folding of the two L-Ser side chains does not induce a direct interaction between them; both O atoms are in fact engaged in intermolecular hydrogen bonds. The molecule can be described as approaching C_2 symmetry.

Hydrogen bonds and intermolecular contacts of interest are listed in Table 3. For each peptide molecule there are four hydrogen bonds, two of the N–H···O type and two of the OH···O type, which connect the DKP rings in spirals parallel to the [001] axis (Fig. 3). The interactions between adjacent spirals are the normal stacking distances of about 3·3 Å (Fig. 1) and the rather short O(1)···N(1) contact (3·07 Å).

References

BALASUBRAMANIAN, D. & WETLAUFER, D. B. (1967). *Conformation of Biopolymers*, Vol. 1, edited by G. N. RAMACHANDRAN, pp. 147–156. New York: Academic Press.

BENEDETTI, E., MARSH, R. E. & GOODMAN, M. (1976). *J. Am. Chem. Soc.* **98**, 6676–6684.

BLOW, D. M. (1976). *Acc. Chem. Res.* **9**, 145–152.

BOCCHI, V., CASNATI, G., DOSSENA, A. & MARCHELLI, R. (1979). *Synthesis*, pp. 961–962.

COTRAIT, M. & PTAK, M. (1978). *Acta Cryst.* B**34**, 528–532.

COTRAIT, M., PTAK, M., BUSETTA, B. & HETZ, A. (1976). *J. Am. Chem. Soc.* **98**, 1073–1076.

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

DEBER, C. M., MADISON, V. & BLOUT, E. R. (1976). *Acc. Chem. Res.* **9**, 106–113.

DECLERCQ, J. P., GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1973). *Acta Cryst.* A**29**, 231–234.

DOSSENA, A., RIZZO, V., MARCHELLI, R., CASNATI, G. & LUISI, P. L. (1976). *Biochim. Biophys. Acta*, **446**, 493–505.

FISHER, E. & JACOBS, W. A. (1906). *Chem. Ber.* **39**, 2942–2950.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.

HRUBY, V. J. (1974). *Chemistry and Biochemistry of Amino Acids, Peptides and Proteins*, Vol. 3, edited by B. WEINSTEIN. New York: Marcel Dekker.

IUPAC–IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1970). *J. Mol. Biol.* **52**, 1–17.

LIN, C. F. & WEBB, L. E. (1973). *J. Am. Chem. Soc.* **95**, 6803–6811.

MARCHELLI, R., DOSSENA, A., POCHINI, A. & DRADI, E. (1977). *J. Chem. Soc. Perkin Trans.* 1, pp. 713–717.

RAMANI, R., VENKATESAN, K. & MARSH, R. E. (1978). *J. Am. Chem. Soc.* **100**, 949–953.

STANFORD, R. H. & WASER, J. (1972). *Acta Cryst.* A**28**, 213–215.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

WILSON, A. J. C. (1942). *Nature (London)*, **150**, 151–152.

Acta Cryst. (1981). B**37**, 629–634

The Structures of Ethyl 1,4,5-*exo*-Trimethyl-7-oxo-2,3-diphenylbicyclo[2.2.1]hept-2-ene-5-*endo*-carboxylate (*A*) and Ethyl 1,4-Dimethyl-7-oxo-2,3-diphenylbicyclo[2.2.1]hept-2-ene-5-*endo*-carboxylate (*B*)

BY S. N. BALASUBRAHMANYAM, R. USHA AND K. VENKATESAN

Department of Organic Chemistry, Indian Institute of Science, Bangalore-560012, *India*

(*Received* 24 *July* 1980; *accepted* 25 *November* 1980)

Abstract

Crystals of $C_{25}H_{26}O_3$ (*A*) are triclinic, space group $P\bar{1}$, with $a = 9{\cdot}197\ (2)$, $b = 10{\cdot}357\ (2)$, $c = 11{\cdot}086\ (3)$ Å, $\alpha = 94{\cdot}07\ (2)$, $\beta = 98{\cdot}21\ (3)$, $\gamma = 90{\cdot}82\ (2)°$, $V = 1042{\cdot}2$ Å^3, $Z = 2$, $D_{obs} = 1{\cdot}19$, $D_{calc} = 1{\cdot}198$ Mg m^{-3} and μ(Cu $K\alpha$) = 0·661 mm^{-1}; $R = 6{\cdot}2\%$ for 2525 significant reflections. Crystals of $C_{24}H_{24}O_3$ (*B*) are monoclinic, space group $P2_1/a$, with $a = 11{\cdot}584\ (2)$, $b = 11{\cdot}315\ (2)$, $c = 15{\cdot}900\ (4)$ Å, $\beta = 104{\cdot}02\ (2)°$, $V = 2022{\cdot}4$ Å^3, $Z = 4$, $D_{obs} = 1{\cdot}19$, $D_{calc} = 1{\cdot}185$ Mg m^{-3} and μ(Mo $K\alpha$) = 0·081 mm^{-1}; $R = 4{\cdot}2\%$ for 1990 significant reflections. The steric strain introduced by the bulky substituents on the norbornenone system is discussed. In addition, a possible relationship between the orientation of the ester function and the anisochrony of its *O*-methylene protons is brought out.

Introduction

The X-ray crystallographic investigations of the title compounds were undertaken in order to verify the hypothesis (Bhaskara Reddy, 1976) that the greater anisochrony exhibited by the *O*-methylene protons of compound *A*, which was in apparent violation of a heuristic developed by Binsch (1973), could have arisen, in part, due to a tilt in the ester axis, C(5)–C(10) (Fig. 1), towards the phenyl rings, caused by changing the substituent from H to methyl at C(5).

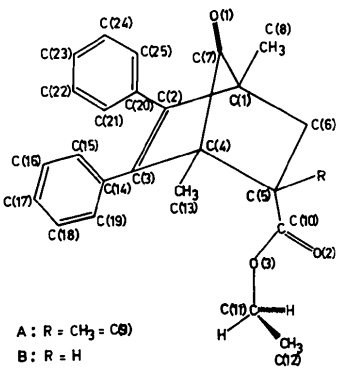


Fig. 1. Numbering of the atoms.

The heuristic developed by Binsch (1973) was for ethanes of the type $XYZCCu_Au_Bu$ and did not take into account possible cyclic connectivity among the ligands *X*, *Y*, *Z*. That it would be violated if such connectivity existed is demonstrated by the compounds *A* and *B*.

Experimental

Preliminary Weissenberg photographs indicated the monoclinic space group $P2_1/a$ for *B* and the triclinic space group *P*1 or $P\bar{1}$ for *A*. Intensity data were collected on a CAD-4 diffractometer with Cu $K\alpha$ and Mo $K\alpha$ radiations for *A* and *B* respectively. The total numbers of reflections collected for *A* and *B* were 3107

0567-7408/81/030629-06$01.00