The bond angles and distances within the pyridinium ring seem normal with angles ranging from 119·2 (4) to 120·4 (3)° and distances ranging from 1·352 (5) to 1·374 (7) Å; the ring is planar to within ±0·005 (5) Å. The *n*-butyl chain exhibits some signs of disorder involving C(9) and C(8) as shown by shortened bonds among the chain carbon atoms and by the instability during least-squares refinement of the H atoms bonded to C(8), C(9) and C(10). The H atoms bonded to C(8), C(9) and C(10) were finally placed in ideal positions and constrained to ride on their attached C atom to enable the least-squares refinement to converge with a reasonable model of the molecular structure.

The *n*-butyl chain is in the extended staggered form with a torsion angle C(7)—C(8)—C(9)—C(10) of 175·3 (5)°. The *n*-butyl chain junction with the pyridinium ring is of non-extended staggered form with the torsion angle N(1)—C(7)—C(8)—C(9) of 44·7 (7)°; therefore, the *n*-butyl chain lies approximately normal to the plane of the pyridinium ring with torsion angles C(2)—N(1)—C(7)—C(8) 81·5 (5) and C(6)—N(1)—C(7)—C(8) −96·9 (5)°.

The chloride ion lies in a hole bounded by the edges of pyridinium rings with five Cl···H contacts in the range 2·553 to 2·720 Å; four *n*-butyl chains give six Cl···H contacts in the range 3·133 to 3·389 Å. The shortest non-H contact with Cl is 3·516 Å and the shortest Cl···Cl distance is 4·794 Å to Cl^- ions at $\pm0{\cdot}5 + x, 0{\cdot}5 - y, -z$.

The authors gratefully acknowledge the support of this work by National Science Foundation grant CHE-8515474. The X-ray diffractometer system was provided by NSF grant CHE-8403823.

References

CROMER, D. T. (1974). *International Tables for X-ray Crystallography*. Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*. Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

FRENZ, B. A. (1978). *The Enraf-Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Determination*. In *Computing and Crystallography*, edited by H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI. Delft Univ. Press.

GALE, R. J. & OSTERYOUNG, R. A. (1983). *Haloaluminates*. In *Molten Salt Techniques*, edited by D. G. LOVERING & R. J. GALE, pp. 55–78. New York: Plenum.

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

RHINEBARGER, R. R. & POPOV, A. I. (1986). *Inorg. Chem.* In the press.

RHINEBARGER, R. R., ROVANG, J. W. & POPOV, A. I. (1984). *Inorg. Chem.* **23**, 2557–2558.

TAULELLE, F. & POPOV, A. I. (1983). *Polyhedron*, **2**, 889–894.

Acta Cryst. (1986). C**42**, 1773–1777

Structures of Three Diels–Alder Adducts of Hexacyclo[$10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}$]-pentadeca-5,7-diene-3,10-dione

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Abstract. (V) Octacyclo[$10.6.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}.0^{13,18}$]henicosa-15,19-diene-3,10,14,17-tetraone, $C_{21}H_{16}O_4$, $M_r = 332{\cdot}4$, monoclinic, $P2_1/m$, $a = 7{\cdot}175$ (1), $b = 11{\cdot}920$ (3), $c = 8{\cdot}622$ (1) Å, $\beta = 100{\cdot}18$ (1)°, $U = 725{\cdot}8$ Å^3, $Z = 2$, $D_m = 1{\cdot}54$, $D_x = 1{\cdot}52$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 9{\cdot}8$ mm^{-1}, $F(000) = 348$, $T = 130$ K, $R = 0{\cdot}042$ for 808 independent observed reflections. (VI) 15-Oxa-octacyclo[$10.5.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}.0^{13,17}$]icos-18-ene-3,10,14,16-tetraone, $C_{19}H_{14}O_5$, $M_r = 322{\cdot}3$, monoclinic, $P2_1/n$, $a = 12{\cdot}521$ (3), $b = 6{\cdot}369$ (2), $c = 17{\cdot}604$ (4) Å, $\beta = 107{\cdot}09$ (2)°, $U = 1342$ Å^3, $Z = 4$, $D_m = 1{\cdot}59$, $D_x = 1{\cdot}60$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 10{\cdot}8$ mm^{-1}, $F(000) = 672$, $T = 130$ K, $R = 0{\cdot}052$ for 1578 independent observed reflections. (VII) 13,14-Bis(methoxycarbonyl)heptacyclo[$10.2.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}$]heptadeca-13,15-diene-3,10-dione, $C_{21}H_{18}O_6$, $M_r = 366{\cdot}4$, monoclinic, $P2_1/c$, $a = 12{\cdot}257$ (4), $b = 6{\cdot}858$ (2), $c = 19{\cdot}610$ (5) Å, $\beta = 90{\cdot}09$ (2)°, $U = 1648$ Å^3, $Z = 4$, $D_m = 1{\cdot}44$, $D_x = 1{\cdot}48$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 10{\cdot}1$ mm^{-1}, $F(000) = 768$, $T = 130$ K, $R = 0{\cdot}038$ for 2104 independent observed reflections. The benzoquinone and maleic anhydride adducts, (V) and (VI), result from Alder attack of the dienophile on the carbonyl-bearing face of the diene, whereas the dimethyl acetylene

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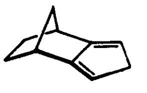
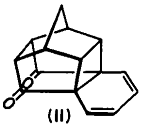
dicarboxylate adduct, (VII), results from dienophile attack on the opposite face of the diene. Comparable bonding geometry in the three structures is similar.

Introduction. π-Facial selectivities observed in the Diels–Alder reactions of isodicyclopentadiene (I) and its derivatives have been the subject of extensive research in recent years (Gleiter & Paquette, 1983; Brown & Houk, 1985; Paquette, Kravetz & Hsu, 1985; and references therein). We are currently engaged in a related study of Diels–Alder reactions of the title diene (II). Dienophile attack on this diene can take place either on the carbonyl-bearing face of the diene, to produce (III), or on the opposite face, to produce (IV). Reaction of diene (II) with benzoquinone has been reported (Tolstikov, Lerman & Galin, 1975; Galin, Afonichev, Lerman, Kazakov & Tolstikov, 1978) and the product formulated, without proof, as that resulting from attack on the face opposite that bearing the carbonyl groups. In contrast the product of the reaction with maleic anhydride was given as that resulting from attack on the carbonyl face (Filipescu & Menter, 1969). Reaction with dimethyl acetylene dicarboxylate gave a product of uncertain stereochemistry (Kushner, 1971; Mehta, Singh & Rao, 1980). We now report unambiguous determinations of the full stereochemistry of these three adducts (V–VII).


(I)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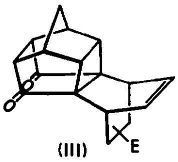
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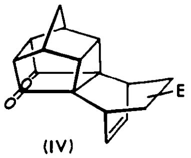
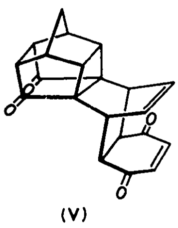


(IV)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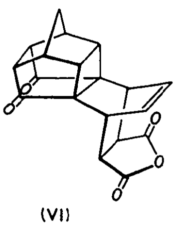
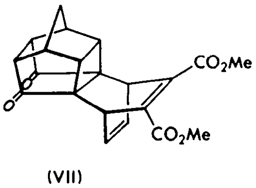

(VI)



(VII)

Experimental. All three compounds were prepared by literature procedures and recrystallized from benzene, (V) and (VI), or benzene–dichloromethane, (VII). Crystal sizes 0·65 × 0·08 × 0·03 mm for (V), 0·53 × 0·35 × 0·03 mm for (VI), 0·70 × 0·50 × 0·04 mm for (VII). D_m by flotation in acidic zinc bromide solutions. Nicolet $R3m$ diffractometer, $\theta/2\theta$ data collection for $3 < 2\theta < 50°$ index ranges: $h \pm 8$, k 0/14, l 0/10 for (V); $h \pm 13$, k 0/7, l 0/20 for (VI); $h \pm 14$, k 0/8, l 0/23 for (VII); lattice parameters from 25 reflections with $20 < 2\theta < 30°$. Standard reflections (and intensity variations): 200, 060, 004 (2·1%) for (V), 301, 020, 014 (2·7%) for (VI), 400, 020, 006 (5·2%) for (VII) monitored every 100 measurements. Reflections measured, unique reflections, $R_{\rm int}$, observed reflections $[I > 3\sigma(I)]$: 1512, 1361, 0·017, 808 for (V), 2794, 2377, 0·048, 1578 for (VI), 3400, 2910, 0·025, 2104 for (VII). Corrections for Lorentz and polarization effects but not for absorption.

All structures solved by direct methods and refined on $|F|$ by blocked cascade least-squares procedures. All non-hydrogen atoms anisotropic, H atoms in calculated positions with isotropic thermal parameters equal to the isotropic equivalent of their carrier carbon (C—H = 0·96 Å). $w^{-1} = [\sigma^2(F) + g(F)^2]$. $R = 0·042$, $wR = 0·042$, $g = 0·0004$, $S = 1·33$, 115 parameters for (V). $R = 0·052$, $wR = 0·055$, $g = 0·0010$, $S = 1·53$, 217 parameters for (VI). $R = 0·038$, $wR = 0·042$, $g = 0·0007$, $S = 1·38$, 244 parameters for (VII). $(\Delta/\sigma)_{\max}$ 0·062 for (V), 0·044 for (VI), 0·092 for (VII). $(\Delta\rho)_{\max} = 0·20$, 0·39, 0·20, $(\Delta\rho)_{\min} = -0·25$, $-0·42$, $-0·26$ e Å^{-3} for (V), (VI), (VII) respectively. Scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations, including diagrams, on a Nova 4X computer using *SHELXTL* (Sheldrick, 1983).

Discussion. Final atom coordinates for the three Diels–Alder adducts (V)–(VII) are listed in Tables 1–3 respectively.* Figs. 1–3 show perspective views of the three structures and include the atom labelling. Although all three compounds possess molecular mirror symmetry, only the benzoquinone adduct (V) has crystallographic mirror symmetry passing through the C(1) carbon bridge.

The structure of the benzoquinone adduct (V) is that resulting from dienophile attack on the carbonyl-bearing face of the diene and is therefore different from that previously proposed (Tolstikov *et al.*, 1975; Galin *et al.*, 1978). Furthermore, the cycloaddition occurs in an Alder manner, presumably stabilized by secondary

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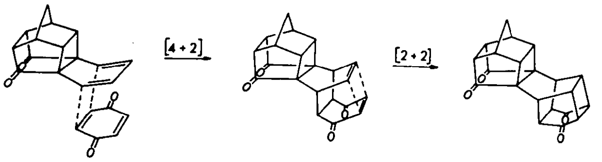
* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43175 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *for* (V) *with e.s.d.'s in parentheses*

	x	*y*	*z*	U_{eq}*
O(4)	3229 (3)	858 (2)	4206 (2)	26 (1)
O(10)	2183 (3)	263 (2)	8970 (3)	46 (1)
C(1)	9070 (6)	2500	3631 (5)	28 (1)
C(2)	7897 (4)	1555 (2)	4143 (3)	23 (1)
C(3)	5856 (4)	1830 (3)	3319 (3)	23 (1)
C(4)	4664 (4)	1410 (2)	4482 (3)	20 (1)
C(5)	5678 (4)	1826 (2)	6065 (3)	20 (1)
C(6)	7804 (4)	1848 (2)	5883 (3)	23 (1)
C(7)	6398 (4)	1944 (3)	8954 (3)	24 (1)
C(8)	5092 (4)	1412 (2)	7582 (3)	21 (1)
C(9)	3048 (4)	1850 (2)	7607 (3)	22 (1)
C(10)	2316 (4)	1279 (3)	8945 (4)	26 (1)
C(11)	1754 (4)	1944 (3)	10216 (4)	30 (1)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

orbital interactions (Ginsburg, 1983). Molecular models show that the *anti*-Alder transition state is highly destabilized by steric interactions. Thus the structure of the known (Tolstikov *et al.*, 1975; Galin *et al.*, 1978) [2 + 2]-photoadduct of (V) should accordingly be reassigned as (VIII), as shown below.



(VIII)

Formation of (VIII) by sequential [4 + 2] and [2 + 2] cycloadditions.

The structure of (V) shows that in the ground state the double bonds that interact in this [2 + 2]-cycloaddition are well separated in space, the C(7)—C(11) interatomic distance being 3·683 (4) Å. The cyclohexenedione ring is planar (to within 0·03 Å) as a result of being fused to a bicyclo[2.2.2]octane system. This is in contrast to the twisted ring conformation found in benzoquinone Diels–Alder adducts of acyclic dienes (see, for example, Paquette, Schaefer & Blount, 1983).

The structure of (VI) (Fig. 2) also corresponds to that resulting from Alder approach of the dienophile on the carbonyl-bearing face of the diene, in agreement with that previously proposed (Filipescu & Menter, 1969). Comparison of bond lengths and angles (Tables 4 and 5) related by the non-crystallographic molecular mirror symmetry shows excellent agreement, mean deviations of related bond lengths and angles being 0·006 Å and 0·7° respectively. As is usual in such adducts (Watson, Galloy, Bartlett & Roof, 1981; Subramanyam, Bartlett, Iglesias, Watson & Galloy, 1982) the five-membered anhydride ring is planar (to within 0·01 Å).

The dimethyl acetylene dicarboxylate adduct (VII) (Fig. 3) results from dienophile attack on the opposite face of the diene. In a previous report (Kushner, 1971) this was considered to be the more probable structure. Again bond lengths and angles related by the non-crystallographic mirror symmetry are in excellent

Table 2. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *for* (VI)

	x	*y*	*z*	U_{eq}*
O(4)	4489 (2)	2868 (4)	3788 (1)	18 (1)
O(4*A*)	7201 (2)	3347 (4)	2958 (1)	22 (1)
O(10)	2111 (2)	2050 (4)	1177 (1)	24 (1)
O(10*A*)	5049 (2)	2751 (4)	271 (1)	32 (1)
O(11)	3435 (2)	2323 (4)	563 (1)	18 (1)
C(1)	6541 (3)	9180 (6)	4430 (2)	19 (1)
C(2)	5488 (3)	7837 (5)	4258 (2)	15 (1)
C(2*A*)	6987 (3)	8153 (6)	3804 (2)	18 (1)
C(3)	5924 (3)	5561 (5)	4307 (2)	16 (1)
C(3*A*)	6981 (3)	5797 (5)	3979 (2)	16 (1)
C(4)	4981 (3)	4457 (5)	3703 (2)	13 (1)
C(4*A*)	6727 (3)	4822 (5)	3161 (2)	15 (1)
C(5)	4716 (3)	5858 (5)	2977 (2)	12 (1)
C(5*A*)	5773 (3)	6105 (5)	2652 (2)	12 (1)
C(6)	4948 (3)	8091 (5)	3345 (2)	15 (1)
C(6*A*)	5979 (3)	8329 (5)	3028 (2)	14 (1)
C(7)	3537 (3)	6970 (5)	1649 (2)	14 (1)
C(7*A*)	4417 (3)	7218 (5)	1379 (2)	14 (1)
C(8)	3683 (3)	5305 (5)	2283 (2)	13 (1)
C(8*A*)	5406 (3)	5792 (5)	1745 (2)	13 (1)
C(9)	3977 (3)	3198 (5)	1937 (2)	14 (1)
C(9*A*)	4985 (3)	3493 (5)	1620 (2)	14 (1)
C(10)	3054 (3)	2490 (5)	1228 (2)	14 (1)
C(10*A*)	4571 (3)	2883 (5)	761 (2)	19 (1)

* See footnote to Table 1.

Table 3. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *for* (VII)

	x	*y*	*z*	U_{eq}*
O(4)	907 (1)	6241 (2)	−357 (1)	29 (1)
O(4*A*)	3892 (1)	5164 (2)	−944 (1)	30 (1)
O(10)	1153 (1)	2149 (2)	2137 (1)	32 (1)
O(10*A*)	4755 (1)	−540 (2)	984 (1)	28 (1)
O(11)	1771 (1)	−647 (2)	1688 (1)	26 (1)
O(11*A*)	3960 (1)	213 (2)	1981 (1)	28 (1)
C(1)	1382 (2)	42 (3)	−1368 (1)	28 (1)
C(2)	822 (2)	1488 (3)	−899 (1)	25 (1)
C(2*A*)	2532 (2)	779 (3)	−1225 (1)	25 (1)
C(3)	1248 (2)	3495 (3)	−1131 (1)	23 (1)
C(3*A*)	2462 (2)	2989 (3)	−1363 (1)	24 (1)
C(4)	1274 (2)	4635 (3)	−469 (1)	21 (1)
C(4*A*)	3246 (2)	3865 (3)	−851 (1)	22 (1)
C(5)	1802 (2)	3266 (3)	35 (1)	19 (1)
C(5*A*)	3009 (2)	2771 (3)	−193 (1)	19 (1)
C(6)	1434 (2)	1211 (3)	−208 (1)	22 (1)
C(6*A*)	2615 (2)	731 (3)	−432 (1)	21 (1)
C(7)	2599 (2)	5640 (3)	801 (1)	24 (1)
C(7*A*)	3607 (2)	5217 (3)	610 (1)	24 (1)
C(8)	1817 (2)	3925 (3)	789 (1)	20 (1)
C(8*A*)	3786 (2)	3116 (3)	417 (1)	20 (1)
C(9)	2335 (2)	2270 (3)	1182 (1)	20 (1)
C(9*A*)	3365 (2)	1865 (3)	998 (1)	18 (1)
C(10)	1696 (2)	1291 (3)	1724 (1)	20 (1)
C(10*A*)	4098 (2)	381 (3)	1303 (1)	21 (1)
C(11)	1298 (2)	−1753 (4)	2240 (1)	33 (1)
C(11*A*)	4558 (2)	−1352 (4)	2302 (1)	36 (1)

* See footnote to Table 1.

agreement (mean deviations 0·005 Å and 0·5° respectively). In this case, however, significant torsional angle differences exist in the relative conformations of the methoxycarbonyl groups (Fig. 3), as is commonly observed in dimethyl acetylene dicarboxylate adducts (Subramanyam *et al.*, 1982; Paquette *et al.*, 1983).

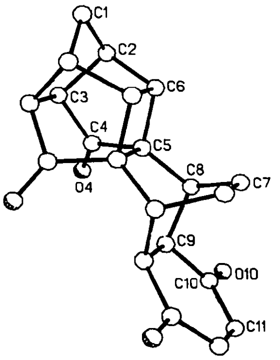


Fig. 1. Perspective view and atom labelling of the benzoquinone adduct (V). Hydrogen atoms omitted for clarity.

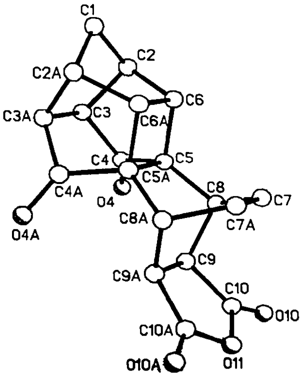


Fig. 2. Perspective view and atom labelling of the maleic anhydride adduct (VI). Hydrogen atoms omitted for clarity.

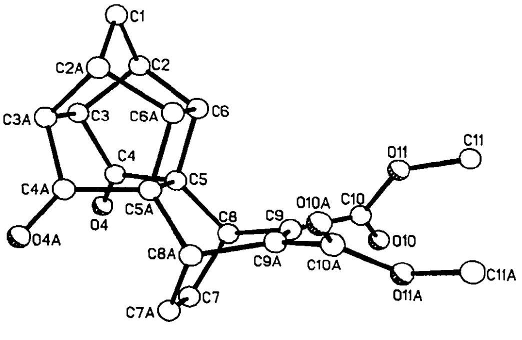


Fig. 3. Perspective view and atom labelling of the dimethyl acetylene dicarboxylate adduct (VII). Hydrogen atoms omitted for clarity.

Table 4. *Comparison of bond lengths* (Å)

	(V)	(VI)	(VII)
C(1)–C(2)	1·518 (4)	1·525 (5)	1·518 (3)
C(1)–C(2*A*)		1·523 (5)	1·523 (5)
C(2)–C(3)	1·546 (4)	1·543 (5)	1·542 (3)
C(2*A*)–C(3*A*)		1·532 (5)	1·542 (3)
C(2)–C(6)	1·554 (4)	1·559 (4)	1·559 (3)
C(2*A*)–C(6*A*)		1·567 (4)	1·558 (3)
C(3)–C(3*A*)	1·596 (6)	1·599 (5)	1·594 (3)
C(3)–C(4)	1·513 (4)	1·510 (4)	1·516 (3)
C(3*A*)–C(4*A*)		1·515 (5)	1·513 (3)
C(4)–O(4)	1·210 (3)	1·216 (4)	1·210 (3)
C(4*A*)–O(4*A*)		1·219 (4)	1·206 (3)
C(4)–C(5)	1·513 (4)	1·513 (4)	1·508 (3)
C(4*A*)–C(5*A*)		1·506 (4)	1·520 (3)
C(5)–C(5*A*)	1·606 (6)	1·597 (5)	1·582 (3)
C(5)–C(6)	1·561 (4)	1·554 (5)	1·554 (3)
C(5*A*)–C(6*A*)		1·553 (5)	1·553 (3)
C(5)–C(8)	1·526 (4)	1·537 (4)	1·546 (3)
C(5*A*)–C(8*A*)		1·539 (4)	1·547 (3)
C(6)–C(6*A*)	1·553 (6)	1·556 (5)	1·548 (3)
C(7)–C(7*A*)	1·326 (6)	1·332 (5)	1·324 (3)
C(7)–C(8)	1·512 (4)	1·512 (4)	1·517 (3)
C(7*A*)–C(8*A*)		1·518 (4)	1·506 (3)
C(8)–C(9)	1·560 (4)	1·562 (5)	1·512 (3)
C(8*A*)–C(9*A*)		1·550 (5)	1·517 (3)
C(9)–C(9*A*)	1·550 (6)	1·534 (5)	1·342 (3)
C(9)–C(10)	1·511 (4)	1·500 (4)	1·482 (3)
C(9*A*)–C(10*A*)		1·499 (4)	1·483 (3)
C(10)–O(10)	1·215 (4)	1·191 (4)	1·203 (2)
C(10*A*)–O(10*A*)		1·188 (5)	1·200 (2)
C(10)–O(11)		1·392 (4)	1·334 (3)
C(10*A*)–O(11*A*)			1·346 (2)
C(10*A*)–O(11)		1·408 (4)	
C(10)–C(11)	1·465 (4)		
C(11)–C(11*A*)	1·325 (6)		
O(11)–C(11)			1·444 (3)
O(11*A*)–C(11*A*)			1·443 (3)

Table 5. *Comparison of bond angles* (°)

	(V)	(VI)*		(VII)*	
C(2)–C(1)–C(2*A*)	95·8	95·4		95·2	
C(1)–C(2)–C(3)	103·8	104·2	104·5	104·5	104·0
C(1)–C(2)–C(6)	103·5	103·6	103·1	103·3	103·6
C(3)–C(2)–C(6)	101·4	101·2	101·3	101·7	101·5
C(2)–C(3)–C(3*A*)	102·3	102·0	102·6	101·9	102·5
C(2)–C(3)–C(4)	103·0	102·0	102·8	102·4	103·8
C(3*A*)–C(3)–C(4)	109·3	110·4	109·9	109·8	108·4
C(3)–C(4)–C(5)	104·6	104·6	104·5	104·4	104·2
C(3)–C(4)–O(4)	127·6	128·3	127·6	128·1	127·5
C(5)–C(4)–O(4)	127·8	127·0	127·8	127·4	128·3
C(4)–C(5)–C(6)	103·7	102·8	103·8	103·9	104·4
C(4)–C(5)–C(5*A*)	109·1	111·2	109·2	110·4	108·3
C(4)–C(5)–C(8)	120·4	117·4	119·3	116·7	117·5
C(5*A*)–C(5)–C(6)	89·0	89·2	89·3	89·4	89·3
C(5*A*)–C(5)–C(8)	108·9	109·3	109·5	108·9	108·9
C(6)–C(5)–C(8)	121·0	123·4	121·5	124·1	124·2
C(2)–C(6)–C(6*A*)	103·0	103·0	102·8	103·2	102·7
C(2)–C(6)–C(5)	107·6	107·8	107·2	107·2	107·6
C(5)–C(6)–C(6*A*)	91·0	90·8	90·7	90·5	90·7
C(7*A*)–C(7)–C(8)	114·8	114·5	115·8	114·5	114·6
C(5)–C(8)–C(7)	108·0	108·5	108·7	104·4	104·6
C(5)–C(8)–C(9)	107·8	105·5	104·8	105·8	106·5
C(7)–C(8)–C(9)	107·7	107·8	107·7	108·0	107·6
C(8)–C(9)–C(9*A*)	109·5	110·5	110·2	114·4	113·9
C(8)–C(9)–C(10)	108·3	111·7	113·0	118·9	119·0
C(9*A*)–C(9)–C(10)	116·8	104·4	105·0	126·7	127·1
C(9)–C(10)–O(10)	120·1	129·7	130·7	123·7	123·9
C(9)–C(10)–C(11)	120·4				
O(10)–C(10)–C(11)	119·5				
C(10)–C(11)–C(11*A*)	122·8				
C(9)–C(10)–C(11)		110·6	109·8	112·1	112·3
O(10)–C(10)–O(11)		119·7	119·4	124·2	123·8
C(10)–O(11)–C(10*A*)		110·1			
C(10)–O(11)–C(11)				117·1	115·4
Ave. e.s.d.	0·3	0·2		0·2	

* For (VI) and (VII) the first value refers to the angle subtended at C(*X*) and the second value to that at C(*XA*).

Comparison of equivalent bond lengths and angles among the three structures again shows good agreement, particularly within the 'Cookson-cage' framework (Cookson, Grundwell, Hill & Hudec, 1964). Two notable features in the bonding geometries of all three structures are the significant bond elongations of the C(5)—C(5*A*) and C(3)—C(3*A*) bonds (Tables 4 and 5), the former being a propellane-type bond and both reflecting the mutual repulsion between the C(4) and C(4*A*) carbonyl groups. Similar effects exist in related structures, which also exhibit similar torsional angles within the cage structure (Marchand, Suri, Earlywine, Powell & van der Helm, 1984; Mehta, Singh, Srikrishna, Cameron & Chan, 1979; Okamoto, Harano, Yasuda, Osawa & Kanematsu, 1983).

References

BROWN, F. K. & HOUK, K. N. (1985). *J. Am. Chem. Soc.* **107**, 1971–1978.

COOKSON, R. C., GRUNDWELL, E., HILL, R. R. & HUDEC, J. (1964). *J. Chem. Soc.* pp. 3064–3075.

FILIPESCU, N. & MENTER, J. M. (1969). *J. Chem. Soc. B*, pp. 616–620.

GALIN, F. Z., AFONICHEV, D. D., LERMAN, B. M., KAZAKOV, V. P. & TOLSTIKOV, G. A. (1978). *Zh. Org. Khim.* **14**, 2308–2317.

GINSBURG, D. (1983). *Tetrahedron*, **39**, 2095–2135.

GLEITER, R. & PAQUETTE, L. A. (1983). *Acc. Chem. Res.* **16**, 328–334.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

KUSHNER, A. S. (1971). *Tetrahedron Lett.* pp. 3275–3278.

MARCHAND, A. P., SURI, S. C., EARLYWINE, A. D., POWELL, D. R. & VAN DER HELM, D. (1984). *J. Org. Chem.* **49**, 670–675.

MEHTA, G., SINGH, V. & RAO, K. S. (1980). *Tetrahedron Lett.* **21**, 1369–1372.

MEHTA, G., SINGH, V., SRIKRISHNA, A., CAMERON, T. S. & CHAN, C. (1979). *Tetrahedron Lett.* pp. 4595–4598.

OKAMOTO, Y., HARANO, K., YASUDA, M., OSAWA, E. & KANEMATSU, K. (1983). *Chem. Pharm. Bull.* **31**, 2526–2529.

PAQUETTE, L. A., KRAVETZ, T. M. & HSU, L.-Y. (1985). *J. Am. Chem. Soc.* **107**, 6598–6603.

PAQUETTE, L. A., SCHAEFER, A. G. & BLOUNT, J. F. (1983). *J. Am. Chem. Soc.* **105**, 3642–3649.

SHELDRICK, G. M. (1983). *SHELXTL Users Manual*, revision 4. Nicolet XRD Corporation, Madison, Wisconsin.

SUBRAMANYAM, R., BARTLETT, P. D., IGLESIAS, G. Y. M., WATSON, W. H. & GALLOY, J. (1982). *J. Org. Chem.* **47**, 4491–4498.

TOLSTIKOV, G. A., LERMAN, B. M. & GALIN, F. Z. (1975). *Zh. Org. Khim.* **11**, 1348–1349.

WATSON, W. H., GALLOY, J., BARTLETT, P. D. & ROOF, A. A. M. (1981). *J. Am. Chem. Soc.* **103**, 2022–2031.

Acta Cryst. (1986). C**42**, 1777–1780

Structures of Dipeptides Trityl-glycyl-L-phenylalanine Benzyl Ester and *tert*-Butyloxycarbonyl-L-phenylalanyl-*S*-ethyl-L-cysteine Dimethylamide

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Abstract. $C_{37}H_{34}N_2O_3$ (I), $M_r = 554{\cdot}68$, monoclinic, $C2$, $a = 26{\cdot}133\ (21)$, $b = 10{\cdot}455\ (8)$, $c = 11{\cdot}809\ (10)$ Å, $\beta = 108{\cdot}88\ (6)^\circ$, $V = 3053\ (4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}207\ (2)$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}827$ cm^{-1}, $F(000) = 1176$, room temperature, $R = 0{\cdot}0462$ for 1259 unique observed reflections. $C_{21}H_{33}N_3O_4S$ (II), $M_r = 423{\cdot}57$, monoclinic, $P2_1$, $a = 9{\cdot}817\ (24)$, $b = 9{\cdot}318\ (8)$, $c = 13{\cdot}641\ (20)$ Å, $\beta = 97{\cdot}65\ (16)^\circ$, $V = 1237\ (4)$ Å^3, $Z = 2$, $D_x = 1{\cdot}137\ (4)$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}609$ cm^{-1}, $F(000) = 456$, room temperature, $R = 0{\cdot}0531$ for 825 unique observed reflections. The values of the torsion angles observed in the peptide group are $\omega = 176{\cdot}68\ (30)$, $\upsilon = -2{\cdot}92\ (25)^\circ$ and $\omega = 174{\cdot}96\ (32)$, $\upsilon = 0{\cdot}00\ (25)^\circ$ for compounds (I) and (II) respectively and demonstrate the peptide bonds to be 'planar and *trans*'. The molecules are interconnected by hydrogen bonds [O(23)···H(20) = 2·427 (83) Å (I); O(22)···H(8) = 1·932 (176), O(18)···H(19) = 2·087 (95) Å (II)].

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