Acta Cryst. (1989). C**45**, 1339–1342

Structures of Two Diastereoisomeric Saturated Polycyclic $C_{22}H_{24}O$ Ketones

By William H. Watson* and Ante Nagl†

Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, *USA*

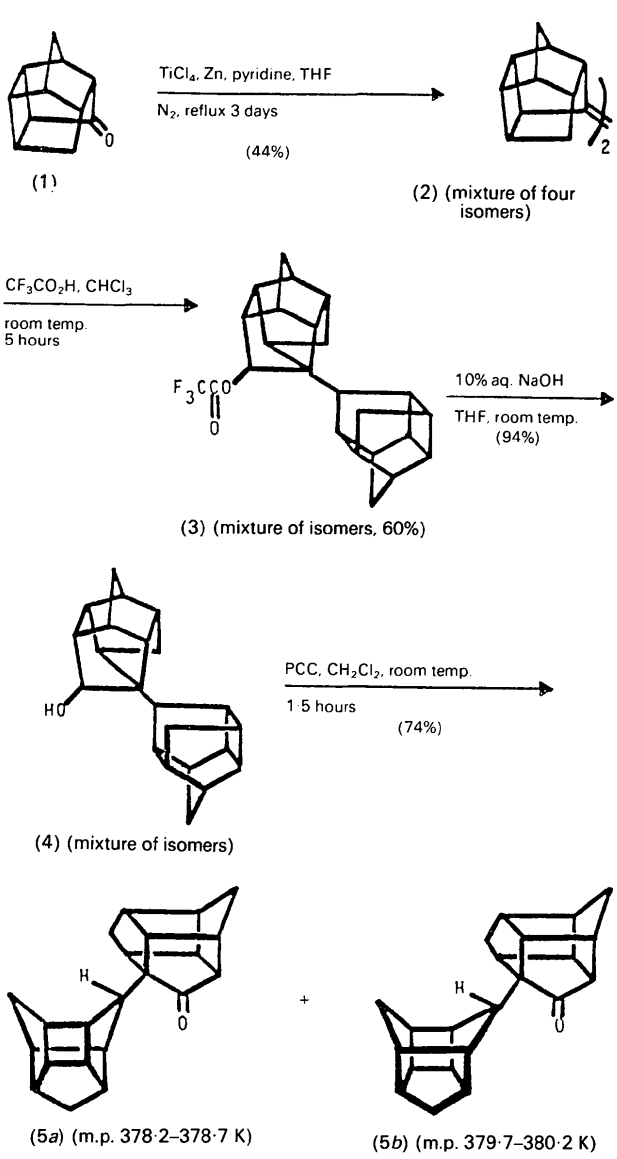
and Alan P. Marchand* and Mahendra N. Deshpande

Department of Chemistry, University of North Texas, PO Box 5068, *Denton, Texas* 76203, *USA*

(*Received* 9 *September* 1988; *accepted* 20 *January* 1989)

Abstract. 3-(Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undec-8-yl)pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-4-one. (5*a*), $M_r = 304{\cdot}44$, triclinic, $P\bar{1}$, $a = 6{\cdot}3469\,(6)$, $b = 11{\cdot}425\,(1)$, $c = 11{\cdot}5724\,(9)$ Å, $\alpha = 63{\cdot}751\,(7)$, $\beta = 82{\cdot}039\,(7)$, $\gamma = 88{\cdot}534\,(8)^\circ$, $V = 744{\cdot}7\,(1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}358$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}75$ cm^{-1}, $F(000) = 328$, $T = 294$ K, $R = 0{\cdot}0392$ for 2372 independent reflections. (5*b*), $M_r = 304{\cdot}44$, triclinic, $P\bar{1}$, $a = 6{\cdot}4193\,(6)$, $b = 10{\cdot}812\,(1)$, $c = 11{\cdot}302\,(1)$ Å, $\alpha = 90{\cdot}180\,(7)$, $\beta = 94{\cdot}073\,(7)$, $\gamma = 105{\cdot}190\,(7)^\circ$, $V = 754{\cdot}8\,(1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}340$ g cm^{-3}, $\lambda(\text{Mo } K\alpha)$, $\mu = 0{\cdot}75$ cm^{-1}, $F(000) = 328$, $T = 300$ K, $R = 0{\cdot}0362$ for 1784 independent reflections. The diastereoisomers consist of a cage composed of six fused five-membered rings containing a ketone moiety bonded to a cage composed of four fused five-membered rings and a four-membered ring. There are no short inter- or intramolecular interactions; however, (5*a*) is more dense than (5*b*) and it is calculated to be 5·2 kJ mol^{-1} less strained.

Introduction. As part of a program that involves the synthesis and chemistry of novel, substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes (Marchand, 1989), the titanium-promoted dimerization (Lenoir, 1977; McMurry, 1983; Pons & Santelli, 1988) of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one [(1); Lerman, Galin, Umanskaya & Tolstikov, 1978] was studied. A mixture of four $C_{22}H_{24}$ dimeric alkenes (2) results from this reaction (Flippen-Anderson, Gilardi, George, Marchand, Jin & Deshpande, 1988). Subsequently, it was found that this mixture of alkene dimers, when reacted with trifluoroacetic acid in chloroform solution at room temperature for five hours, afforded unreacted dimers (two isomers, 17%) plus a mixture of isomeric rearranged trifluoroacetates [(3), Scheme 1, 60% yield]. Hydrolysis of the mixture of trifluoroacetate esters with 10% aqueous sodium hydroxide at room temperature yielded a mixture of isomeric alcohols, (4), which upon pyridinium chlorochromate (PCC) promoted oxidation afforded a mixture of the diastereoisomeric ketones [(5*a*) and (5*b*), 70% yield]. Separation of (5*a*) and



Scheme 1

---

* Authors to whom correspondence should be addressed.

† On leave from Faculty of Technology, University of Zagreb, Zagreb, Yugoslavia.

(*5b*) was accomplished by using flash column chromatography (silica-gel stationary phase, ethyl acetate–hexane mixed solvent as eluent). The structure of each isomer was elucidated by a single-crystal X-ray structural analysis.

Experimental. A single crystal of (*5a*), m.p. 378·2–378·7 K, was obtained by careful fractional recrystallization from an ethyl acetate–hexane mixed solvent. A single crystal of (*5b*), m.p. 379·7–380·2 K, was obtained by careful fractional recrystallization from hexane. [An intimate mixture of *ca* 1:1 (*5a*) and (*5b*) displayed m.p. 369–373 K.] An $R3m/\mu$ update of a Nicolet $P2_1$ diffractometer with graphite-monochromated Mo $K\alpha$ radiation was used for all measurements. Data were collected in the ω mode (2θ fixed, ω varied). Lorentz–polarization corrections and a ψ-scan-based empirical absorption correction were applied. The structures were solved by direct methods and refined by block-cascade least-squares procedures. H atoms were located in difference maps and refined with isotropic thermal parameters. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. All programs were supplied by Nicolet (Nicolet Instrument Corporation, 1986) for Desktop 30 Microeclipse and Nova 4/C configuration. Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974).

A colorless crystal of (*5a*) of dimensions 0·28 × 0·43 × 0·50 mm; $3{\cdot}0 \leq 2\theta \leq 50°$, variable scan rate (4–29·3° min^{-1}); lattice parameters from least-squares refinement of 25 reflections ($26{\cdot}32 \leq 2\theta \leq 28{\cdot}81°$); no systematic absences and statistics consistent with space group $P\bar{1}$; monitored reflections $0\bar{3}4$ and $\bar{3}32$ showed no statistically significant changes in intensities; 2626 independent reflections measured ($-7 \leq h \leq 7$, $-11 \leq k \leq 13$, $0 \leq l \leq 13$), $2372 \geq 3\sigma(I)$; transmission factors 0·903 to 0·969; $R = 0{\cdot}0392$, $wR = 0{\cdot}0540$ for 305 parameters and 2372 reflections ($R = 0{\cdot}0432$ and $wR = 0{\cdot}0545$ for all 2626 independent reflections), $S = 2{\cdot}248$, $(\Delta/\sigma)_{\max} = 0{\cdot}014$; largest peaks in the final difference map of $-0{\cdot}16$ and 0·24 e Å^{-3}; g set to 0·00029 in weighting scheme, isotropic extinction correction k $\{F = F_c/[1{\cdot}0 + 0{\cdot}002kF_c^2/\sin(2\theta)]^{0{\cdot}25}\}$ refined to value of 0·00544. Table 1 lists atomic positional parameters while bond lengths and bond angles are given in Tables 3 and 4. Fig. 1 is a drawing of compound (*5a*).

Table 1. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* (Å^2 × 10^3) *for compound* (*5a*)

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

	x	*y*	*z*	*U*
C(1)	6146 (2)	3420 (1)	−576 (1)	30 (1)
C(2)	8198 (2)	3053 (1)	112 (1)	29 (1)
C(3)	7303 (2)	2345 (1)	1612 (1)	29 (1)
C(4)	8365 (2)	1040 (1)	2011 (1)	39 (1)
O(4)	9364 (2)	431 (1)	2882 (1)	65 (1)
C(5)	7976 (2)	759 (1)	901 (1)	39 (1)
C(6)	9166 (2)	1943 (1)	−237 (1)	36 (1)
C(7)	8117 (2)	2057 (1)	−1383 (1)	38 (1)
C(8)	5898 (2)	2199 (1)	−785 (1)	33 (1)
C(9)	5656 (2)	1154 (1)	676 (1)	34 (1)
C(10)	5059 (2)	1965 (1)	1470 (1)	31 (1)
C(11)	4324 (2)	3247 (1)	489 (1)	31 (1)
C(1′)	9548 (2)	4170 (1)	3435 (1)	36 (1)
C(2′)	9126 (2)	3069 (2)	4845 (1)	39 (1)
C(3′)	6778 (3)	3120 (2)	5371 (1)	43 (1)
C(4′)	5926 (3)	1728 (2)	5873 (2)	57 (1)
C(5′)	6684 (3)	1633 (1)	4604 (1)	43 (1)
C(6′)	9055 (2)	2037 (1)	4316 (1)	38 (1)
C(7′)	9466 (2)	3132 (1)	2897 (1)	32 (1)
C(8′)	7405 (2)	3193 (1)	2325 (1)	28 (1)
C(9′)	5789 (2)	2838 (1)	3553 (1)	35 (1)
C(10′)	5873 (2)	3889 (2)	4087 (1)	38 (1)
C(11′)	7572 (3)	4962 (1)	3284 (1)	40 (1)

Table 2. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* (Å^2 × 10^3) *for compound* (*5b*)

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

	x	*y*	*z*	*U*
C(1)	234 (3)	−1661 (2)	2844 (2)	50 (1)
C(2)	1232 (3)	−1079 (2)	1681 (2)	38 (1)
C(3)	3423 (2)	−102 (1)	2125 (1)	32 (1)
C(4)	5077 (2)	−608 (2)	1523 (1)	33 (1)
O(4)	6675 (2)	−33 (1)	1057 (1)	45 (1)
C(5)	4177 (3)	−2013 (2)	1681 (2)	41 (1)
C(6)	1907 (3)	−2221 (2)	1081 (2)	46 (1)
C(7)	659 (3)	−3411 (2)	1678 (2)	57 (1)
C(8)	1145 (3)	−2826 (2)	2917 (2)	51 (1)
C(9)	3605 (3)	−2101 (2)	2995 (1)	40 (1)
C(10)	3660 (2)	−674 (2)	3364 (1)	38 (1)
C(11)	1488 (3)	−803 (2)	3849 (2)	47 (1)
C(1′)	1923 (3)	3220 (2)	1882 (2)	44 (1)
C(2′)	2934 (3)	3859 (2)	3084 (2)	46 (1)
C(3′)	5362 (3)	4424 (2)	2966 (2)	52 (1)
C(4′)	6462 (4)	3891 (2)	3983 (2)	67 (1)
C(5′)	5220 (3)	2495 (2)	3702 (2)	49 (1)
C(6′)	2851 (3)	2522 (2)	3603 (2)	47 (1)
C(7′)	1836 (2)	1872 (2)	2396 (2)	40 (1)
C(8′)	3540 (2)	1307 (1)	1897 (1)	33 (1)
C(9′)	5577 (2)	2296 (2)	2396 (2)	40 (1)
C(10′)	5658 (3)	3660 (2)	1866 (2)	49 (1)
C(11′)	3677 (3)	3644 (2)	1050 (2)	52 (1)

A colorless crystal of (*5b*) of dimensions 0·23 × 0·50 × 0·50 mm; $3 \leq 2\theta \leq 45°$, variable scan rate (4–29·3° min^{-1}); lattice parameters from least-squares refinement of 25 reflections ($25{\cdot}70 \leq 2\theta \leq 29{\cdot}57°$); no systematic absences and statistics consistent with space group $P\bar{1}$; monitored reflections $\bar{1}5\bar{2}$ and $\bar{3}10$ showed no statistically significant changes in intensities; 1969 independent reflections measured ($-6 \leq h \leq 6$, $-11 \leq k \leq 11$, $0 \leq l \leq 12$), $1784 \geq 3\sigma(I)$; transmission factors 0·865 to 0·896; $R = 0{\cdot}0362$, $wR = 0{\cdot}0498$ for 304 parameters and 1784 reflections ($R = 0{\cdot}0400$, $wR = 0{\cdot}0506$ for all 1969 independent reflections), $S = 1{\cdot}696$, $(\Delta/\sigma)_{\max} = 0{\cdot}037$; largest peaks in final difference map of $-0{\cdot}18$ and 0·15 e Å^{-3}; g set to 0·00058 in weighting scheme. Table 2 lists atomic positional parameters while

Table 3. *Bond lengths* (Å) *for compounds* (5*a*) *and* (5*b*)

	(5*a*)	(5*b*)		(5*a*)	5(*b*)
C(1)—C(2)	1·572 (2)	1·565 (3)	C(10)—C(11)	1·514 (2)	1·507 (2)
C(1)—C(8)	1·532 (2)	1·521 (3)	C(1′)—C(2′)	1·548 (2)	1·541 (2)
C(1)—C(11)	1·515 (2)	1·507 (2)	C(1′)—C(7′)	1·569 (3)	1·559 (2)
C(2)—C(3)	1·581 (2)	1·570 (2)	C(1′)—C(11′)	1·512 (2)	1·498 (3)
C(2)—C(6)	1·579 (2)	1·577 (3)	C(2′)—C(3′)	1·540 (2)	1·533 (2)
C(3)—C(4)	1·521 (2)	1·515 (2)	C(2′)—C(6′)	1·554 (3)	1·551 (3)
C(3)—C(10)	1·550 (2)	1·547 (2)	C(3′)—C(4′)	1·516 (3)	1·501 (3)
C(3)—C(8′)	1·533 (2)	1·528 (2)	C(3′)—C(10′)	1·538 (2)	1·540 (3)
C(4)—O(4)	1·198 (2)	1·208 (2)	C(4′)—C(5′)	1·530 (3)	1·531 (2)
C(4)—C(5)	1·506 (3)	1·493 (2)	C(5′)—C(6′)	1·532 (2)	1·525 (3)
C(5)—C(6)	1·528 (2)	1·524 (2)	C(5′)—C(9′)	1·539 (2)	1·533 (3)
C(5)—C(9)	1·552 (2)	1·552 (2)	C(6′)—C(7′)	1·552 (2)	1·552 (2)
C(6)—C(7)	1·519 (2)	1·515 (2)	C(7′)—C(8′)	1·533 (2)	1·524 (2)
C(7)—C(8)	1·519 (2)	1·513 (3)	C(8′)—C(9′)	1·530 (2)	1·527 (2)
C(8)—C(9)	1·568 (2)	1·564 (2)	C(9′)—C(10′)	1·580 (3)	1·583 (2)
C(9)—C(10)	1·577 (2)	1·588 (2)	C(10′)—C(11′)	1·520 (2)	1·513 (3)

Table 4. *Bond angles* (°) *for compounds* (5*a*) *and* (5*b*)

	(5*a*)	(5*b*)
C(2)—C(1)—C(8)	98·7 (1)	98·8 (1)
C(2)—C(1)—C(11)	105·6 (1)	106·2 (1)
C(8)—C(1)—C(11)	103·1 (1)	103·3 (1)
C(1)—C(2)—C(3)	104·1 (1)	104·4 (1)
C(1)—C(2)—C(6)	103·6 (1)	104·0 (1)
C(3)—C(2)—C(6)	105·5 (1)	105·1 (1)
C(2)—C(3)—C(4)	100·7 (1)	102·5 (1)
C(2)—C(3)—C(10)	97·2 (1)	97·1 (1)
C(4)—C(3)—C(10)	100·5 (1)	98·7 (1)
C(2)—C(3)—C(8′)	114·2 (1)	115·3 (1)
C(4)—C(3)—C(8′)	123·0 (1)	114·7 (1)
C(10)—C(3)—C(8′)	116·9 (1)	124·9 (1)
C(3)—C(4)—O(4)	132·1 (2)	129·8 (1)
C(3)—C(4)—C(5)	99·3 (1)	100·0 (1)
O(4)—C(4)—C(5)	128·4 (2)	130·3 (2)
C(4)—C(5)—C(6)	99·6 (1)	101·0 (1)
C(4)—C(5)—C(9)	105·3 (1)	103·4 (1)
C(6)—C(5)—C(9)	99·2 (1)	99·1 (1)
C(2)—C(6)—C(5)	99·1 (1)	99·4 (1)
C(2)—C(6)—C(7)	105·2 (1)	104·8 (1)
C(5)—C(6)—C(7)	102·8 (1)	102·2 (1)
C(6)—C(7)—C(8)	94·3 (1)	94·7 (1)
C(1)—C(8)—C(7)	103·3 (1)	103·8 (2)
C(1)—C(8)—C(9)	98·2 (1)	98·1 (1)
C(7)—C(8)—C(9)	105·8 (1)	105·3 (1)
C(5)—C(9)—C(8)	103·6 (1)	103·7 (1)
C(5)—C(9)—C(10)	104·2 (1)	104·3 (1)
C(8)—C(9)—C(10)	104·3 (1)	104·1 (1)
C(3)—C(10)—C(9)	100·8 (1)	100·2 (1)
C(3)—C(10)—C(11)	102·6 (1)	103·8 (1)
C(9)—C(10)—C(11)	104·4 (1)	103·7 (1)
C(1)—C(11)—C(10)	94·8 (1)	94·6 (1)
C(2′)—C(1′)—C(7′)	89·9 (1)	90·4 (1)
C(2′)—C(1′)—C(11′)	104·4 (1)	104·5 (1)
C(7′)—C(1′)—C(11′)	112·6 (1)	112·5 (1)
C(1′)—C(2′)—C(3′)	107·3 (1)	107·7 (1)
C(1′)—C(2′)—C(6′)	90·2 (1)	90·1 (1)
C(3′)—C(2′)—C(6′)	103·1 (1)	102·4 (1)
C(2′)—C(3′)—C(4′)	103·6 (1)	105·0 (2)
C(2′)—C(3′)—C(10′)	100·3 (1)	99·9 (1)
C(4′)—C(3′)—C(10′)	104·9 (1)	104·8 (1)
C(3′)—C(4′)—C(5′)	94·8 (1)	94·7 (1)
C(4′)—C(5′)—C(6′)	103·7 (1)	104·1 (2)
C(4′)—C(5′)—C(9′)	104·3 (1)	104·1 (1)
C(6′)—C(5′)—C(9′)	100·9 (1)	100·7 (1)
C(2′)—C(6′)—C(5′)	102·8 (1)	103·2 (1)
C(2′)—C(6′)—C(7′)	90·3 (1)	90·2 (1)
C(5′)—C(6′)—C(7′)	107·0 (1)	107·1 (1)
C(1′)—C(7′)—C(6′)	89·5 (1)	89·3 (1)
C(1′)—C(7′)—C(8′)	111·5 (1)	111·3 (1)
C(6′)—C(7′)—C(8′)	105·8 (1)	106·2 (1)
C(3)—C(8′)—C(7′)	115·4 (1)	118·2 (1)
C(3)—C(8′)—C(9′)	116·4 (1)	116·9 (1)
C(7′)—C(8′)—C(9′)	99·4 (1)	99·2 (1)
C(5′)—C(9′)—C(8′)	104·5 (1)	105·4 (1)
C(5′)—C(9′)—C(10′)	102·5 (1)	102·2 (1)
C(8′)—C(9′)—C(10′)	111·1 (1)	110·3 (1)
C(3′)—C(10′)—C(9′)	102·4 (1)	102·1 (1)
C(3′)—C(10′)—C(11′)	103·1 (1)	103·5 (2)
C(9′)—C(10′)—C(11′)	112·5 (1)	112·2 (1)
C(1′)—C(11′)—C(10′)	100·7 (1)	100·8 (1)

bond lengths and bond angles are given in Tables 3 and 4. Fig. 2 is a drawing of compound (5*b*).*

Discussion. The two diastereoisomers (5*a*) and (5*b*) consist of a cage composed of six fused five-membered rings containing a ketone moiety bonded to a cage composed of four fused five-membered rings and a four-membered ring. Both of these cages contain a norbornane fragment. The diastereoisomers crystallize in the triclinic space group $P\bar{1}$; however (5*a*) is slightly more dense (1·358 g cm^{-3}) than (5*b*) (1·340 g cm^{-3}) indicating (5*a*) is packed more efficiently. There are no short inter- or intramolecular interactions and the melting points of the two C_{22} compounds are relatively low ($\sim$379 K).

While there are no significant inter- or intramolecular interactions, several chemically equivalent bonds and angles in the two structures differ from each other by more than 3σ. Some differences might

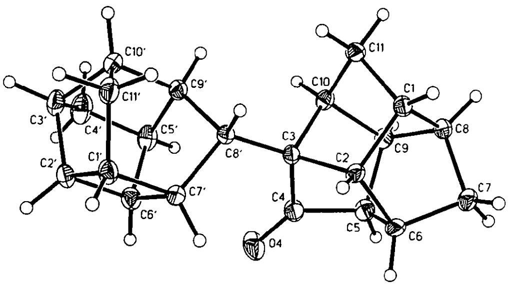


Fig. 1. Compound (5*a*) with thermal ellipsoids drawn at the 25% probability level. H atoms are represented by spheres of arbitrary size.

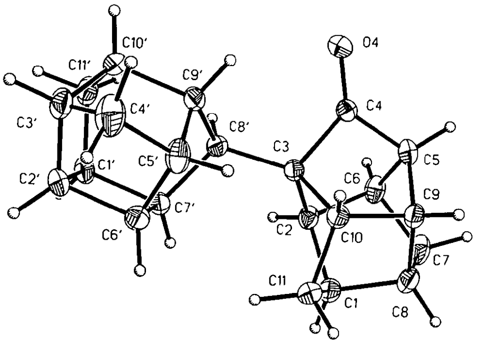


Fig. 2. Compound (5*b*) with thermal ellipsoids drawn at the 25% probability level. H atoms are represented by spheres of arbitrary size.

---

* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors for compounds (5*a*) and (5*b*) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51896 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

be expected to occur around the diastereometric linkages between the two cages; however, the remainder of the molecules should be equivalent. Molecular mechanics calculations (*MM*2; Allinger & Yuh, 1980) indicate that (5*a*) is about 5·2 kJ mol^{-1} less strained than (5*b*), ΔH_f = 53·0 and 58·2 kJ mol^{-1} for (5*a*) and 5(*b*), respectively. While bond-length and bond-angle differences between (5*a*) and 5(*b*) in the calculated structures are not as large as those observed, the trends about the linking atoms are similar. The two elongated bonds in each structure, C(1′)—C(7′) = 1·569 (3) and 1·559 (2) Å and C(9′)—C(10′) = 1·580 (3) and 1·583 (2) Å in (5*a*) and 5(*b*), respectively, are consistent with values observed for the parent cage and its derivatives (Watson, Nagl, Marchand & Reddy, 1989; Marchand, Arney, Gilardi & Flippen-Anderson, 1987; Marchand, Annapurna, Reddy, Watson & Nagl, 1988). In the other half of the molecule the ketone moiety imposes some geometric constraints, and internal strain is relieved partially by the elongation of four bonds to distances longer than 1·565 Å.

We thank The Welch Foundation (Grant P-074 to WHW, Grant B-963 to APM), the Air Force Office of Scientific Research (Grant AFOSR-88-0132 to APM), and the Faculty Research Committees of Texas Christian University and the University of North Texas for partial financial support of this study.

References

Allinger, N. L. & Yuh, Y. H. (1980). *MM*2 and *MMPI* subroutines for IBM PC. Updated by L. C. Rohren (1984); adapted by J. J. Gajewski & K. E. Gilbert from copy supplied by O. Nelson & C. Scott Owen. Obtained from Serena Software, 489 Serena Lane, Bloomington, IN 47401, USA.

Flippen-Anderson, J. L., Gilardi, R., George, C., Marchand, A. P., Jin, P.-W. & Deshpande, M. N. (1988). *Acta Cryst.* **C44**, 1617–1619.

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

Lenoir, D. (1977). *Synthesis*, pp. 553–554.

Lerman, B. M., Galin, F. Z., Umanskaya, L. A. & Tolstikov, G. A. (1978). *J. Org. Chem. USSR*, **14**, 2536–2541.

Marchand, A. P. (1989). *Advances in Theoretically Interesting Molecules;* Vol. 1, edited by R. P. Thummel, pp. 357–397. Greenwich, CT: JAI Press.

Marchand, A. P., Annapurna, P., Reddy, S. P., Watson, W. H. & Nagl, A. (1988). *J. Org. Chem.* **54**, 187–193.

Marchand, A. P., Arney, B. E. Jr, Gilardi, R. & Flippen-Anderson, J. L. (1987). *J. Org. Chem.* **52**, 3455–3457.

McMurry, J. E. (1983). *Acc. Chem. Res.* **16**, 405–411; and references cited therein.

Nicolet Instrument Corporation (1986). *SHELXTL* for Desktop 30 (Microeclipse). PN-269-1040340. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Pons, J.-M. & Santelli, M. (1988). *Tetrahedron*, **44**, 4295–4312; and references cited therein.

Watson, W. H., Nagl, A., Marchand, A. P. & Reddy, G. M. (1989). *Acta Cryst.* C. Accepted.

Acta Cryst. (1989). **C45**, 1342–1346

A Diels–Alder Cycloadduct of Methylcyclopentadiene with 2,6-Dimethyl-*p*-benzoquinone and the Intramolecular Photocyclization Product of this Cycloadduct

By William H. Watson,* Ante Nagl† and Ram P. Kashyap

Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, *USA*

and Alan P. Marchand* and Dalian Zhao

Department of Chemistry, University of North Texas, PO Box 5068, *Denton, Texas* 76203, *USA*

(*Received* 18 *November* 1988; *accepted* 24 *January* 1989)

Abstract. 3,4a,6-Trimethyl-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione, (1*b*), $C_{14}H_{16}O_2$, M_r = 216·28, monoclinic, $P2_1/a$, a = 11·291 (1), b = 8·267 (1), c = 12·860 (1) Å, β = 107·20 (1)°, V = 1146·6 (2) Å^3, Z = 4, D_x = 1·253 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 0·77 cm^{-1}, F(000) = 464, T = 295 K, R = 0·0445 for 1279 reflections. 1,2,10-Trimethylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione, (2), $C_{14}H_{16}O_2$, M_r = 216·28, orthorhombic, *Pcab*, a = 10·998 (2), b = 11·828 (2), c = 17·179 (2) Å, V = 2234·5 Å^3, Z = 8, D_x = 1·286 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 0·79 cm^{-1}, F(000) = 928, T = 295 K, R = 0·0378 for 1186 observed reflections. Structure (1*b*) contains a norbornene moiety fused to a cyclohexenedione ring. The two sets of C atoms which are joined in the photochemical reaction to form the four-membered ring in (2) are separated by

---

* Authors to whom correspondence should be addressed.

† On leave of absence from the Faculty of Science, University of Zagreb, Yugoslavia.

0108-2701/89/091342-05$03.00