This is also commonly observed for the metal complex (Bousseau, Valade, Legros, Cassoux, Garbauskas & Interrante, 1986; Groeneveld, Schuller, Kramer, Haasnoot & Reedijk, 1986), but there is no obvious explanation for this effect.

The variation in bond lengths observed between the different metal complexes probably reflects differences in intermolecular S···S interactions. In BTDTT there is only one S···S contact less than 3·7 Å [S(4)···S(4, $1-x$, $-y$, $2-z$), 3·535 (1) Å, whereas in BTDTO there are three weak S···S interactions at [S(3)···S(4, $-x$, $\frac{1}{2}+y$, $-z$), 3·592 (2), S(2)···S(5, $1-x$, $\frac{1}{2}+y$, $1-z$), 3·664 (2) and S(2)···S(5, $1-x$, $\frac{1}{2}+y$, $-z$), 3·681 (2) Å].

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Structure of a Dimer Ketone* Formed *via* Fe(CO)$_5$-Promoted Coupling of 7-(*p*-Cyanophenoxy)norbornadiene to Carbon Monoxide

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Abstract. (*syn,syn*)-1,4,4aα,4bβ,5,8,8aβ,9aα-Octahydro-10,11-di(*p*-cyanophenoxy)-1,4:5,8-dimethanofluoren-9-one, $C_{29}H_{22}N_2O_3$, $M_r = 446·53$, triclinic, $P\bar{1}$, $a = 10·186$ (2), $b = 11·148$ (2), $c = 12·052$ (2) Å, $\alpha = 110·36$ (2), $\beta = 109·90$ (2), $\gamma = 98·68$ (2)°, $V = 1148·8$ (4) Å^3, $Z = 2$, $D_x = 1·29$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·79$ mm^{-1}, $F(000) = 468$, $T = 225$ K, final $R = 0·041$ for 2399 observed reflections. The central five-membered ring is planar with normal bond lengths and angles. The norbornene rings are fused to the central ring in an *anti* fashion and are under considerable strain showing both bond lengths (C—C distances as long as 1·559 Å) and angles (C—C—C angles as small as 94·2°) which deviate significantly from normal values.

Introduction. As part of an ongoing study of the thermal reactions of iron carbonyls with 7-substituted norbornadienes (Marchand & Hayes, 1977; Marchand, Earlywine & Heeg, 1986), the reactions of Fe(CO)$_5$ and of Fe$_2$(CO)$_9$ with 7-(*p*-cyanophenoxy)norbornadiene (1) were investigated. Compound (1) was synthesized *via* palladium(II)-

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* (*syn,syn*)-1,4,4aα,4bβ,5,8,8aβ,9aα-Octahydro-9-oxo-1,4:5,8-dimethanofluoren-10,11-diylbis(*p*-oxybenzonitrile).

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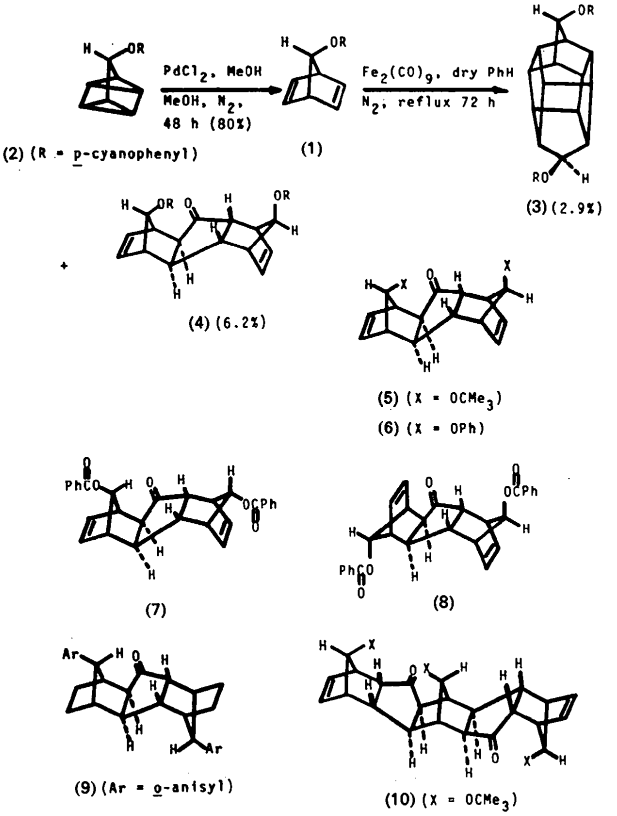
promoted valence isomerization (Patrick & Bechtold, 1984) of 3-(*p*-cyanophenoxy)quadricylane [(2) (Watson, Tavanaiepour, Marchand & Dave, 1987; Marchand & Dave, 1989)]. Thermal reaction of (1) with $Fe(CO)_5$, performed in refluxing di-*n*-butyl ether, resulted primarily in alkyl–oxygen cleavage in the substrate, thereby affording *p*-cyanophenol in 23% yield (Marchand & Dave, 1989). The corresponding reaction of (1) with $Fe_2(CO)_9$, performed in refluxing benzene, afforded unreacted (1) (56%), a cage dimer [(3), 2·9%], and a dimer ketone [(4), 6·2%]. The structure of (4), (*syn,syn*)-1,4,4a*α*,4b*β*,-5,8,8a*β*,9a*α*-octahydro-10,11-di(*p*-cyanophenoxy)-1,4:5,8-dimethanofluoren-9-one, was elucidated by single crystal X-ray structural analysis. A good quality, colorless single crystal of (4), m.p. 470–472 K, was obtained *via* careful fractional crystallization from ethyl acetate–hexane mixed solvent.



(2) (R = p-cyanophenyl)
(1)
(3) (2.9%)
(4) (6.2%)
(5) (X = OCMe$_3$)
(6) (X = OPh)
(7)
(8)
(9) (Ar = o-anisyl)
(10) (X = OCMe$_3$)

Experimental. Colorless, 0·32 × 0·24 × 0·48 mm data crystal. Automated Nicolet *R*3*m*V diffractometer with an incident-beam graphite monochromator; 25 centered reflections within $22 < 2\theta < 30°$ used for determining cell parameters. Data corrected for Lorentz and polarization effects, absorption ignored, $2\theta_{\max} = 45°$; range of *hkl*: $0 \le h \le 10$, $-11 \le k \le 11$, $-13 \le l \le 12$; standards 400, 040, 004, monitored every 100 reflections with random variation 2·5% over data collection, θ–2θ mode, scan width $(1{\cdot}8 + D_{\alpha1\alpha2})$, scan rate a function of count rate (minimum 16, maximum 30° $\min^{-1}$); 3216 reflections measured, 2907 unique, $R_{\rm int} = 0{\cdot}023$, 2399 observed $[F_o > 3\sigma(F_o)]$.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* ($Å^2 \times 10^3$)

	x	*y*	*z*	$U_{\rm eq}$*
C(1)	2400 (3)	7772 (2)	6474 (2)	48 (1)
C(1*A*)	2778 (3)	9331 (2)	6995 (2)	43 (1)
C(2)	2210 (4)	7249 (3)	5079 (2)	58 (2)
C(3)	989 (3)	7414 (3)	4385 (3)	61 (2)
C(4)	306 (3)	8029 (3)	5292 (2)	51 (1)
C(4*A*)	1320 (3)	9502 (2)	6203 (2)	45 (1)
C(5)	800 (3)	10281 (2)	7191 (2)	43 (1)
O(5)	−367 (2)	10523 (2)	6908 (2)	56 (1)
C(5*A*)	1934 (3)	10737 (2)	8570 (2)	41 (1)
C(6)	2719 (3)	12281 (2)	9339 (2)	46 (1)
C(7)	3271 (3)	12737 (2)	8496 (2)	53 (1)
C(8)	4349 (3)	12225 (3)	8413 (3)	55 (1)
C(9)	4545 (3)	11415 (3)	9196 (2)	48 (1)
C(9*A*)	3183 (3)	10135 (2)	8459 (2)	42 (1)
C(10)	765 (3)	7333 (3)	6187 (2)	50 (1)
C(11)	4178 (3)	12271 (3)	10287 (2)	49 (1)
O(12)	409 (2)	7872 (2)	7281 (1)	49 (1)
O(13)	4042 (2)	11574 (2)	11062 (1)	50 (1)
C(14)	781 (3)	7401 (2)	8216 (2)	44 (1)
C(15)	511 (3)	8030 (3)	9294 (3)	52 (1)
C(16)	910 (3)	7688 (3)	10326 (3)	53 (1)
C(17)	1567 (3)	6670 (2)	10270 (2)	51 (1)
C(18)	1792 (3)	6017 (3)	9175 (3)	56 (2)
C(19)	1407 (3)	6371 (2)	8147 (3)	52 (1)
C(20)	2047 (3)	6319 (3)	11347 (3)	68 (2)
N(20)	2489 (3)	6035 (3)	12192 (3)	98 (2)
C(21)	3751 (3)	12184 (2)	12113 (2)	45 (1)
C(22)	3600 (3)	13459 (3)	12508 (2)	52 (1)
C(23)	3374 (3)	14000 (3)	13626 (2)	55 (1)
C(24)	3298 (3)	13289 (2)	14349 (2)	50 (1)
C(25)	3403 (3)	11992 (3)	13926 (3)	56 (2)
C(26)	3623 (3)	11445 (3)	12809 (2)	53 (1)
C(27)	3138 (3)	13909 (3)	15534 (3)	58 (1)
N(27)	3016 (3)	14429 (2)	16484 (2)	74 (1)

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

Structure solved by direct methods. The least-squares refinement used the full-matrix program provided with the MicroVAX versions of the *SHELXTL* system (Sheldrick, 1980). $\sum w(|F_o| - |F_c|)^2$ was minimized where $w = 1/[\sigma^2(|F_o|) + g(F_o)^2]$, $g = 0{\cdot}00025$, secondary isotropic extinction from $F_c^* = F_c/[1{\cdot}0 + 0{\cdot}002(p)F_o^2/\sin 2\theta]^{0{\cdot}25}$ where $p = 0{\cdot}0029\,(4)$. 396 parameters refined: atom coordinates for all atoms, anisotropic temperature factors for non-H atoms and isotropic temperature factors for H atoms; $(\Delta/\sigma)_{\max} = 0{\cdot}01$, $R = 0{\cdot}041$, $wR = 0{\cdot}045$, $S = 1{\cdot}57$. Final difference Fourier excursions 0·20 and $-0{\cdot}14$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).† Atom numbering for Tables 1 and 2, atom coordinates, bond distances and bond angles, follows that shown in Fig. 1.

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† Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52476 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

C(1)—C(1A)	1·561 (3)	C(1)—C(2)	1·506 (3)
C(1)—C(10)	1·542 (4)	C(1A)—C(4A)	1·550 (3)
C(1A)—C(9A)	1·542 (3)	C(2)—C(3)	1·323 (4)
C(3)—C(4)	1·513 (4)	C(4)—C(4A)	1·559 (3)
C(4)—C(10)	1·528 (3)	C(4A)—C(5)	1·517 (3)
C(5)—O(5)	1·219 (3)	C(5)—C(5A)	1·511 (3)
C(5A)—C(6)	1·559 (3)	C(5A)—C(9A)	1·549 (3)
C(6)—C(7)	1·505 (3)	C(6)—C(11)	1·540 (3)
C(7)—C(8)	1·330 (4)	C(8)—C(9)	1·504 (3)
C(9)—C(9A)	1·559 (3)	C(9)—C(11)	1·533 (3)
C(10)—O(12)	1·439 (3)	C(11)—O(13)	1·434 (3)
O(12)—C(14)	1·367 (2)	O(13)—C(21)	1·368 (3)
C(14)—C(15)	1·387 (3)	C(14)—C(19)	1·386 (3)
C(15)—C(16)	1·375 (3)	C(16)—C(17)	1·396 (3)
C(17)—C(18)	1·383 (3)	C(17)—C(20)	1·434 (4)
C(18)—C(19)	1·378 (3)	C(20)—N(20)	1·139 (3)
C(21)—C(22)	1·384 (3)	C(21)—C(26)	1·386 (3)
C(22)—C(23)	1·386 (3)	C(23)—C(24)	1·378 (3)
C(24)—C(25)	1·390 (3)	C(24)—C(27)	1·431 (3)
C(25)—C(26)	1·382 (3)	C(27)—N(27)	1·149 (3)

C(2)—C(1)—C(1A)	106·1 (2)	C(10)—C(1)—C(1A)	102·7 (2)
C(10)—C(1)—C(2)	97·5 (2)	C(4A)—C(1A)—C(1)	102·3 (2)
C(9A)—C(1A)—C(1)	116·7 (2)	C(9A)—C(1A)—C(4A)	107·8 (2)
C(3)—C(2)—C(1)	107·7 (2)	C(4)—C(3)—C(2)	108·0 (2)
C(4A)—C(4)—C(3)	106·3 (2)	C(10)—C(4)—C(3)	97·7 (2)
C(10)—C(4)—C(4A)	101·5 (2)	C(4)—C(4A)—C(1A)	103·6 (2)
C(5)—C(4A)—C(1A)	106·4 (2)	C(5)—C(4A)—C(4)	113·7 (2)
O(5)—C(5)—C(4A)	124·4 (2)	C(5A)—C(5)—C(4A)	110·9 (2)
C(5A)—C(5)—O(5)	124·7 (2)	C(6)—C(5A)—C(5)	115·1 (2)
C(9A)—C(5A)—C(5)	106·6 (2)	C(9A)—C(5A)—C(6)	103·9 (2)
C(7)—C(6)—C(5A)	107·8 (2)	C(11)—C(6)—C(5A)	99·1 (2)
C(11)—C(6)—C(7)	98·8 (2)	C(8)—C(7)—C(6)	107·7 (2)
C(9)—C(8)—C(7)	108·0 (2)	C(9A)—C(9)—C(8)	107·9 (2)
C(11)—C(9)—C(8)	98·9 (2)	C(11)—C(9)—C(9A)	100·6 (2)
C(5A)—C(9A)—C(1A)	107·9 (2)	C(9)—C(9A)—C(1A)	115·4 (2)
C(9)—C(9A)—C(5A)	102·1 (2)	C(4)—C(10)—C(1)	94·3 (2)
O(12)—C(10)—C(1)	116·2 (2)	O(12)—C(10)—C(4)	110·1 (2)
C(9)—C(11)—C(6)	94·2 (2)	O(13)—C(11)—C(6)	115·1 (2)
O(13)—C(11)—C(9)	109·7 (2)	C(14)—O(12)—C(10)	118·6 (2)
C(21)—O(13)—C(11)	119·0 (2)	C(15)—C(14)—O(12)	115·9 (2)
C(19)—C(14)—O(12)	124·3 (2)	C(19)—C(14)—C(15)	119·7 (2)
C(16)—C(15)—C(14)	121·1 (2)	C(17)—C(16)—C(15)	119·2 (2)
C(18)—C(17)—C(16)	119·4 (2)	C(20)—C(17)—C(16)	120·8 (2)
C(20)—C(17)—C(18)	119·7 (2)	C(19)—C(18)—C(17)	121·3 (2)
C(18)—C(19)—C(14)	119·2 (2)	N(20)—C(20)—C(17)	176·6 (3)
C(22)—C(21)—O(13)	124·3 (2)	C(26)—C(21)—O(13)	115·7 (2)
C(26)—C(21)—C(22)	119·9 (2)	C(23)—C(22)—C(21)	119·2 (2)
C(24)—C(23)—C(22)	121·1 (3)	C(25)—C(24)—C(23)	119·4 (2)
C(27)—C(24)—C(23)	119·4 (2)	C(27)—C(24)—C(25)	121·2 (2)
C(26)—C(25)—C(24)	119·8 (3)	C(25)—C(26)—C(21)	120·5 (2)
N(27)—C(27)—C(24)	178·7 (3)		

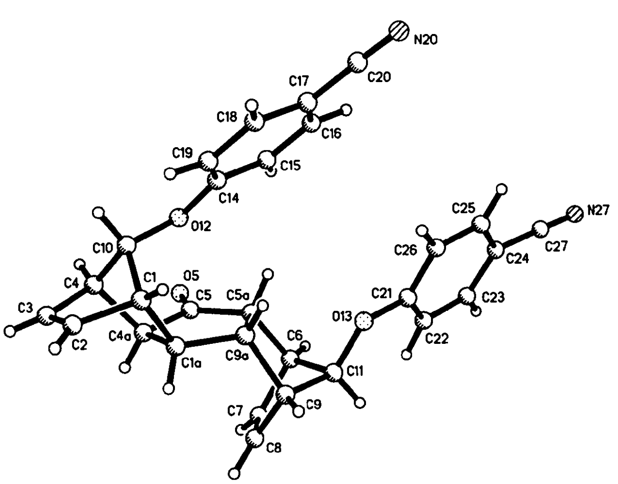

Fig. 1. View of (4) with the atom numbering.

Discussion. The central five-membered ring is planar (±0·05 Å) with normal bond lengths and angles. The norbornene rings are fused to the central ring in an *anti* fashion and are under considerable strain. All internal angles in the norbornene moieties are smaller than normal. At the bridgehead atoms C(10) and C(11) these angles average only 94·2 (2)° while the eight sp^3—sp^3—sp^3 angles average 98·2 (2)° and the four sp^3—sp^2—sp^3 angles average 107·8 (2)°. Further strain is evidenced by the four C—C bonds to the central ring which have an average length of 1·559 (3) Å while the remaining C—C single bonds average 1·533 (3) Å. Similar effects have been observed in the structures of several other related polycyclic ketones such as (5) (Ealick & van der Helm, 1975), (6) (Watson, Marchand & Dave, 1988), (7) and (8) (Marchand, Earlywine & Heeg, 1986), (9) (Marchand, Goodin, Hossain & van der Helm, 1984) and (10) (Ealick, van der Helm, Hayes & Marchand, 1978). In (4), both —O—C_6H_4—C≡N moieties are planar and on the same side of the polycyclic ring system. The closest C···C intermolecular approaches are C(27)···C(4) at 3·44 Å and C(27)···C(22) and C(23)···C(23) both at 3·48 Å.

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