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Structures of 5,9-Diphenyl-7*H*-dibenzo[*a*,*c*]cyclononene, $C_{29}H_{22}$, and 5,9-Diphenyl-7*H*-dibenzo[*a*,*c*]cyclononen-7-one, $C_{29}H_{20}O$

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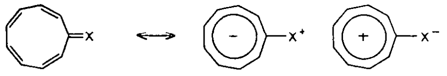
Abstract. $C_{29}H_{22}$: $M_r = 370{\cdot}5$, $P2_1/n$, $a = 11{\cdot}419$ (1), $b = 23{\cdot}694$ (3), $c = 7{\cdot}696$ (2) Å, $\beta = 90{\cdot}53$ (1)°, $V = 2082{\cdot}1$ Å^3, $Z = 4$, $D_x = 1{\cdot}182$ Mg m^{-3}, $F(000) = 784$, $R = 0{\cdot}045$ for 2303 observed reflections. $C_{29}H_{20}O$: $M_r = 384{\cdot}5$, $P\bar{1}$, $a = 10{\cdot}196$ (4), $b = 12{\cdot}163$ (4), $c = 9{\cdot}999$ (4) Å, $\alpha = 113{\cdot}47$ (3), $\beta = 104{\cdot}86$ (2), $\gamma = 67{\cdot}25$ (2)°, $V = 1041{\cdot}4$ Å^3, $Z = 2$, $D_x = 1{\cdot}226$ Mg m^{-3}, $F(000) = 404$, $R = 0{\cdot}041$ for 2641 observed reflections. For both compounds λ(Mo $K\alpha$) = 0·71069 Å, $T = 294$ K. The structures were solved with direct methods and refined with full-matrix least-squares techniques. The nine-membered rings show substantial distortion from a planar conformation as a result of severe steric interactions between the adjacent annelated benzene rings. It is suggested that the various bond twists isolate the C_6H_4–C_6H_4 and C=C–X–C=C fragments from each other, and that this effect stabilizes the molecules compared to the normally less stable cyclononatetraenes.

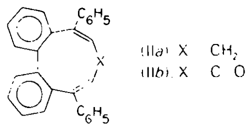
Introduction. Derivatives of cyclononatetraene possessing an exocyclic double bond (I*a*) may show aromatic or antiaromatic characteristics due to resonance contributions of structures like (I*b*) and (I*c*).



(I*a*) (I*b*) (I*c*)

Although the unsubstituted cyclononatetraenes are unstable at room temperature, Rabinovitz and co-workers (Rabinovitz, Bergmann & Gazit, 1971; Rabinovitz & Gazit, 1972, 1978) utilized the 5,9-diphenyldibenzo[*a*,*c*]cyclononene (II) framework to prepare a number of stable nine-membered-ring-containing compounds.

We have determined the crystal structures of the cyclononatetraene (II*a*) and annulenone (II*b*) derivatives for the following reasons: (1) to investigate the effect of a change in the C hybridization at X from sp^3 in (II*a*) to sp^2 in (II*b*) on the ring conformation and structure; (2) to investigate the consequences of the double benzene annelation because it seemed likely that this region of the molecule would show substantial deviations from the overall planarity suggested by the simple structure drawn for (II) above. (II*a*) and (II*b*) will be referred to as $NONCH_2$ and NONCO, respectively, in the following discussion.



Experimental. The compounds were synthesized at the Hebrew University of Jerusalem (Rabinovitz, Bergmann & Gazit, 1971). The solvents used for crystal growing and the dimensions of the specimens used in the X-ray measurements are: $NONCH_2$, benzene–hexane, 0·13 × 0·30 × 0·53 mm; NONCO, methanol, 0·2 × 0·4 × 0·5 mm. A Picker FACS-I diffractometer and Mo radiation (graphite monochromator, $2\theta = 12{\cdot}16°$) were used for all cell-parameter and intensity measurements. The lattice constants were refined by the method of least squares with the Bragg angles obtained from manual centering at $\pm 2\theta$ (estimated to 0·001°). For NONCO, the type I reduced cell (Mighell, Santoro & Donnay, 1969) with all angles < 90° is $a = 9{\cdot}999$, $b = 10{\cdot}196$, $c = 12{\cdot}163$ Å, $\alpha = 67{\cdot}25$, $\beta = 66{\cdot}53$, $\gamma = 75{\cdot}14°$. The specific techniques used in the measurement of X-ray diffraction data in our laboratory have been described previously (Ammon, 1973). Intensity data were measured with the θ–2θ scan method at 2° min^{-1} in 2θ, 10–20 s stationary background counts at the beginning and end of each scan, maximum $2\theta = 50°$; three standard reflections monitored at 100 reflection intervals were used to correct for intensity fluctuations. Total number of data measured, unique data and 'observed' data [$I \geq 3\sigma(I)$] are: $NONCH_2$, 4102, 3677, 2303; NONCO, 3962, 3829, 2641. $NONCH_2$ was

0108-2701/83/030400-04$01.50

Table 1. *Atomic coordinates, temperature factors* (Å^2) *and e.s.d.'s for* NONCH$_2$ *and* NONCO

An asterisk denotes $U_{\rm eq}$, the equivalent value of the anisotropic temperature factor coefficients, calculated from the expression: $U_{\rm eq} = (1/3)\sum_{ij}(U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j)$. The U_{ij} values have been deposited. The e.s.d. of the last significant digit is given in parentheses.

	x	*y*	*z*	*U*
(*a*) NONCH$_2$				
C(1)	0·1322 (2)	−0·06538 (9)	0·2180 (3)	0·051 (6)*
C(2)	0·1753 (2)	−0·0350 (1)	0·3567 (3)	0·071 (6)*
C(3)	0·2644 (2)	0·0038 (1)	0·3304 (3)	0·047 (3)*
C(4)	0·3107 (2)	0·0107 (1)	0·1638 (3)	0·040 (3)*
C(4a)	0·2704 (2)	−0·02072 (9)	0·0240 (3)	0·038 (4)*
C(5)	0·3266 (2)	−0·0099 (1)	−0·1495 (3)	0·034 (4)*
C(6)	0·3852 (2)	−0·0469 (1)	−0·2465 (3)	0·051 (4)*
C(7)	0·4128 (2)	−0·1092 (1)	−0·2279 (4)	0·063 (5)*
C(8)	0·3841 (2)	−0·1423 (1)	−0·0660 (3)	0·052 (5)*
C(9)	0·2782 (2)	−0·16401 (9)	−0·0334 (3)	0·041 (5)*
C(9a)	0·1775 (2)	−0·1439 (1)	−0·1385 (3)	0·039 (7)*
C(10)	0·1326 (2)	−0·1749 (1)	−0·2775 (4)	0·046 (8)*
C(11)	0·0373 (2)	−0·1554 (1)	−0·3701 (4)	0·040 (7)*
C(12)	−0·0145 (2)	−0·1050 (1)	−0·3230 (3)	0·049 (2)*
C(13)	0·0304 (2)	−0·0734 (1)	−0·1859 (3)	0·046 (6)*
C(13a)	0·1274 (2)	−0·09190 (9)	−0·0960 (3)	0·036 (7)*
C(13b)	0·1764 (2)	−0·05837 (9)	0·0499 (3)	0·042 (6)*
C(14)	0·3167 (2)	0·0495 (1)	−0·2123 (3)	0·033 (8)*
C(15)	0·4097 (2)	0·0777 (1)	−0·2902 (3)	0·049 (8)*
C(16)	0·3958 (2)	0·1314 (1)	−0·3572 (4)	0·062 (9)*
C(17)	0·2887 (3)	0·1580 (1)	−0·3473 (4)	0·060 (9)*
C(18)	0·1953 (2)	0·1316 (1)	−0·2651 (4)	0·061 (9)*
C(19)	0·2098 (2)	0·0779 (1)	−0·1975 (3)	0·051 (8)*
C(20)	0·2501 (2)	−0·2035 (1)	0·1110 (3)	0·047 (9)*
C(21)	0·3370 (2)	−0·2295 (1)	0·2100 (4)	0·08 (1)*
C(22)	0·3063 (3)	−0·2685 (1)	0·3406 (4)	0·11 (1)*
C(23)	0·1915 (3)	−0·2830 (1)	0·3703 (4)	0·09 (1)*
C(24)	0·1057 (2)	−0·2583 (1)	0·2742 (4)	0·07 (1)*
C(25)	0·1345 (2)	−0·2190 (1)	0·1456 (4)	0·058 (7)*
H(1)	0·065 (1)	−0·0919 (8)	0·238 (2)	0·049 (6)
H(2)	0·144 (2)	−0·0417 (9)	0·473 (3)	0·073 (7)
H(3)	0·296 (2)	0·029 (1)	0·426 (3)	0·094 (9)
H(4)	0·381 (2)	0·0404 (9)	0·142 (3)	0·074 (7)
H(6)	0·421 (2)	−0·0329 (8)	−0·360 (3)	0·055 (6)
H(7*a*)	0·375 (2)	−0·1280 (8)	−0·334 (3)	0·072 (7)
H(7*b*)	0·498 (2)	−0·1146 (9)	−0·245 (3)	0·072 (7)
H(8)	0·453 (2)	−0·1506 (8)	0·015 (3)	0·060 (6)
H(10)	0·168 (2)	−0·2105 (8)	−0·311 (3)	0·058 (6)
H(11)	0·007 (2)	−0·1789 (9)	−0·474 (3)	0·075 (7)
H(12)	−0·084 (2)	−0·0931 (8)	−0·385 (3)	0·069 (7)
H(13)	−0·005 (1)	−0·0356 (7)	−0·155 (2)	0·039 (5)
H(15)	0·488 (2)	0·0567 (8)	−0·298 (3)	0·062 (7)
H(16)	0·471 (2)	0·1493 (9)	−0·415 (3)	0·076 (7)
H(17)	0·278 (2)	0·197 (1)	−0·398 (3)	0·102 (9)
H(18)	0·110 (2)	0·152 (1)	−0·255 (3)	0·098 (9)
H(19)	0·139 (2)	0·0587 (8)	−0·140 (3)	0·071 (7)
H(21)	0·420 (2)	−0·218 (1)	0·185 (3)	0·092 (8)
H(22)	0·374 (2)	−0·280 (1)	0·411 (4)	0·13 (1)
H(23)	0·165 (2)	−0·313 (1)	0·459 (3)	0·12 (1)
H(24)	0·018 (2)	−0·267 (1)	0·296 (3)	0·097 (8)
H(25)	0·069 (2)	−0·2001 (9)	0·076 (3)	0·077 (7)
(*b*) NONCO				
O(1)	0·6255 (2)	−0·2828 (1)	−0·1163 (2)	0·073 (8)*
C(1)	−0·0032 (2)	−0·0469 (2)	−0·2543 (2)	0·057 (6)*
C(2)	−0·0538 (2)	0·0603 (2)	−0·1362 (2)	0·075 (6)*
C(3)	0·0323 (2)	0·1338 (2)	−0·0540 (2)	0·071 (6)*
C(4)	0·1686 (2)	0·1007 (2)	−0·0877 (2)	0·052 (5)*
C(4a)	0·2219 (2)	−0·0090 (2)	−0·2049 (2)	0·046 (5)*
C(5)	0·3667 (2)	−0·0387 (2)	−0·2427 (2)	0·040 (6)*
C(6)	0·4806 (2)	−0·1411 (2)	−0·2333 (2)	0·053 (7)*
C(7)	0·5014 (2)	−0·2333 (2)	−0·1630 (2)	0·040 (1)*
C(8)	0·3918 (2)	−0·2751 (2)	−0·1417 (2)	0·046 (2)*
C(9)	0·2977 (2)	−0·3233 (1)	−0·2462 (2)	0·044 (2)*
C(9a)	0·2679 (2)	−0·3135 (1)	−0·3957 (2)	0·038 (4)*
C(10)	0·3147 (2)	−0·4208 (2)	−0·5169 (2)	0·049 (5)*
C(11)	0·2846 (2)	−0·4136 (2)	−0·6559 (2)	0·051 (5)*
C(12)	0·2034 (2)	−0·2997 (2)	−0·6781 (2)	0·050 (5)*
C(13)	0·1541 (2)	−0·1925 (2)	−0·5585 (2)	0·049 (5)*
C(13a)	0·1867 (2)	−0·1983 (1)	−0·4177 (2)	0·038 (5)*
C(13b)	0·1341 (2)	−0·0825 (1)	−0·2893 (2)	0·047 (5)*
C(14)	0·3844 (2)	0·0544 (2)	−0·2926 (2)	0·051 (6)*
C(15)	0·5165 (2)	0·0734 (2)	−0·2670 (3)	0·081 (7)*
C(16)	0·5327 (3)	0·1575 (2)	−0·3170 (3)	0·107 (7)*
C(17)	0·4193 (3)	0·2251 (2)	−0·3915 (3)	0·099 (7)*
C(18)	0·2852 (3)	0·2101 (2)	−0·4162 (3)	0·094 (7)*
C(19)	0·2692 (2)	0·1256 (2)	−0·3647 (2)	0·069 (6)*
C(20)	0·2188 (2)	−0·3914 (2)	−0·2195 (2)	0·044 (2)*
C(21)	0·2723 (2)	−0·4523 (2)	−0·1156 (2)	0·061 (4)*
C(22)	0·1[illegible]59 (3)	−0·5134 (2)	−0·0911 (2)	0·077 (4)*
C(23)	0·0634 (3)	−0·5143 (2)	−0·1695 (2)	0·067 (4)*
C(24)	0·0088 (2)	−0·4558 (2)	−0·2736 (2)	0·057 (3)*
C(25)	0·0857 (2)	−0·3960 (2)	−0·3003 (2)	0·049 (3)*
H(1)	−0·070 (2)	−0·097 (1)	−0·312 (2)	0·059 (4)
H(2)	−0·155 (2)	0·083 (2)	−0·114 (2)	0·073 (5)
H(3)	−0·003 (2)	0·209 (2)	0·033 (2)	0·073 (5)
H(4)	0·231 (2)	0·154 (2)	−0·028 (2)	0·073 (5)
H(6)	0·574 (2)	−0·153 (2)	−0·267 (2)	0·077 (6)
H(8)	0·410 (2)	−0·283 (1)	−0·041 (2)	0·061 (4)
H(10)	0·368 (1)	−0·501 (1)	−0·497 (2)	0·055 (4)
H(11)	0·319 (2)	−0·490 (2)	−0·743 (2)	0·078 (5)
H(12)	0·179 (2)	−0·293 (1)	−0·781 (2)	0·064 (5)
H(13)	0·094 (2)	−0·110 (1)	−0·579 (2)	0·057 (4)
H(15)	0·602 (2)	0·024 (2)	−0·207 (2)	0·098 (6)
H(16)	0·628 (2)	0·174 (2)	−0·296 (2)	0·120 (8)
H(17)	0·431 (2)	0·289 (2)	−0·433 (2)	0·114 (8)
H(18)	0·202 (2)	0·259 (2)	−0·481 (2)	0·108 (7)
H(19)	0·171 (2)	0·115 (2)	−0·382 (2)	0·080 (5)
H(21)	0·374 (2)	−0·455 (2)	−0·065 (2)	0·070 (5)
H(22)	0·245 (2)	−0·561 (2)	−0·018 (2)	0·097 (6)
H(23)	0·010 (2)	−0·565 (2)	−0·151 (2)	0·100 (7)
H(24)	−0·088 (2)	−0·454 (2)	−0·329 (2)	0·090 (6)
H(25)	0·047 (2)	−0·352 (1)	−0·375 (2)	0·061 (5)

solved with the direct-methods subprogram *PHASE* in the XRAY 76 system of crystallographic programs (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). A similar approach was not successful with the annulenone, and the structure was solved, following some preliminary symbolic addition carried out by hand, with the program *PHASER* (Ammon, 1964). The least-squares structure refinement used the method of full matrix least squares and minimized the function $\sum w(F_o - F_c)^2$, $w = 1/\sigma^2(F)$; calculations were carried out with anisotropic temperature factors for C and O, and isotropic terms for H (initial positions for these atoms calculated with a C—H distance of 1·0 Å), and included corrections for isotropic secondary extinction (Larson, 1970); only those data for which $I_c > 3\sigma(I_o)$ were used in the least-squares calculations; scattering factors for C and H were generated from the analytical expressions of Cromer & Mann (1968), while those for H were interpolated from the tabulated values of Stewart, Davidson & Simpson (1965). The final *R*, weighted *R*, *S* values and the average shift/error ratios are: NONCH$_2$, 0·045, 0·041, 2·1, 0·3; NONCO, 0·041, 0·046, 7·1, 0·3. The maximum and minimum values in the final difference electron density maps are: NONCH$_2$, 0·18, −0·25 e Å^{-3}; NONCO, 0·25, −0·26 e Å^{-3}. All calculations performed at the University of Maryland's Computer Science Center on a Univac 1108 computer, primarily with the XRAY 76 programs (Stewart *et al.*, 1976); molecular drawings made with the *ORTEP* II (Johnson, 1971) link in XRAY 76; the VDOS system (Lenhert, 1975) was used for diffractometer control.

Discussion. The atomic coordinates are listed in Table 1.* *ORTEP* drawings are given in Fig. 1, and a

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* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38257 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

combined list of bond lengths and angles may be found in Table 2. A key to the atom numbering is given in Fig. 2. The drawings are to the same scale and the molecules have been given almost identical orientations to emphasize their structural similarities. The *ORTEP* views illustrate quite clearly that the nine-membered rings are not planar, and this information is presented in a more quantitative way in the form of the ring bond torsion (dihedral) angles. The major factor responsible for distortion in the nine-membered ring stems from steric interactions between the adjacent, annelated benzene nuclei. The benzene rings adopt an almost perpendicular, biphenyl-like conformation, as a result of severe steric repulsions that would exist between atoms *ortho* to the inter-ring bond [C(13a)–C(13b)] in a planar structure. The C(13a)–C(13b) torsion angles are 85–86°; the average nonbonded distance of 3·32 (4) Å between the appropriate pairs of C atoms *ortho* to C(13a)–C(13b) is slightly shorter than the 3·4 Å van der Waals approach for aromatic rings. Despite this severe distortion, the benzene rings are planar and there are no abnormal bond lengths or angles. A least-squares, best-molecular-fit (Nyburg, 1974) comparison of the C–C_6H_4–C_6H_4–C fragments in the two molecules showed that they are similar, with an average difference of 0·034 Å between corresponding atomic positions.

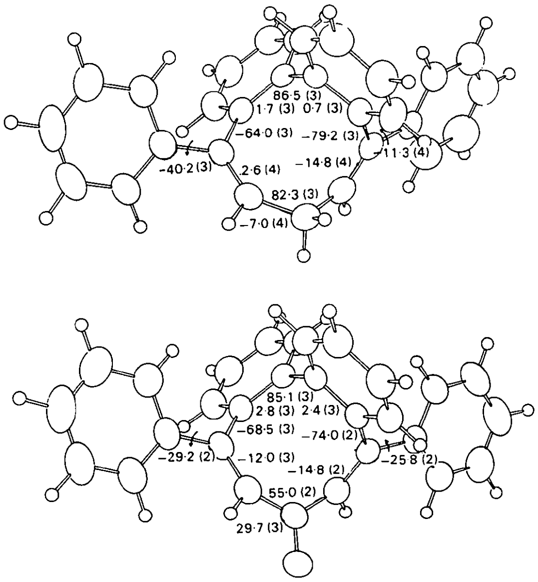

Fig. 1. *ORTEP* drawings of NONCH$_2$ and NONCO made to the same scale. 50% ellipses are used for C and O, and the H atoms are represented with 0·1 Å radius spheres. Some torsion angles (°) are shown.

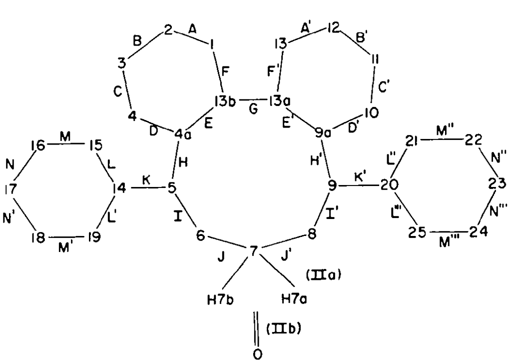

Fig. 2. Atomic and bond labeling key.

Table 2. *Bond lengths* (Å), *angles* (°) *and e.s.d.'s*

Bonds are denoted by the letters *A–N* (see Fig. 2 for key). The distances and angles from similar regions in each structure have been listed together. For example, the distances listed on the *A* line are for bonds *A* and *A'*, whereas those found on the *L* lines are for *L*, *L'* (upper) and *L''*, *L'''* (lower).

	NONCH$_2$	NONCO
Bonds		
A	1·374 (4), 1·388 (4)	1·388 (2), 1·393 (2)
B	1·387 (4), 1·383 (4)	1·377 (3), 1·385 (3)
C	1·401 (4), 1·375 (4)	1·381 (3), 1·375 (3)
D	1·383 (3), 1·392 (4)	1·403 (2), 1·398 (2)
E	1·411 (3), 1·398 (3)	1·395 (3), 1·398 (3)
F	1·403 (3), 1·372 (3)	1·390 (3), 1·384 (3)
G	1·482 (3), —	1·499 (2), —
H	1·509 (3), 1·479 (3)	1·489 (3), 1·491 (3)
I	1·336 (3), 1·339 (4)	1·352 (2), 1·338 (2)
J	1·516 (4), 1·511 (4)	1·472 (4), 1·483 (4)
K	1·490 (3), 1·491 (3)	1·488 (4), 1·485 (3)
L	1·396 (3), 1·401 (3),	1·396 (3), 1·388 (3),
	1·389 (4), 1·398 (4)	1·391 (3), 1·399 (3)
M	1·382 (4), 1·384 (3),	1·380 (5), 1·394 (4),
	1·412 (5), 1·400 (4)	1·382 (4), 1·385 (4)
N	1·378 (5), 1·392 (4),	1·371 (4), 1·396 (5),
	1·375 (5), 1·355 (4)	1·379 (4), 1·373 (4)
C(7)–O	—	1·230 (2)
Angles		
A–B	119·4 (2), 120·6 (2)	119·6 (2), 119·5 (2)
A–F	121·7 (2), 120·1 (2)	121·0 (2), 120·8 (2)
B–C	119·6 (2), 119·6 (2)	120·4 (2), 120·1 (1)
C–D	121·6 (2), 120·3 (2)	120·5 (2), 121·0 (2)
D–E	118·6 (2), 119·7 (2)	119·1 (2), 119·0 (2)
D–H	117·1 (2), 122·0 (2)	119·1 (2), 120·4 (2)
E–F	119·1 (2), 119·6 (2)	119·5 (1), 119·6 (1)
E–G	121·0 (2), 119·8 (2)	120·3 (2), 119·8 (2)
E–H	124·2 (2), 118·3 (2)	121·6 (1), 120·4 (1)
F–G	119·9 (2), 120·5 (2)	120·2 (2), 120·6 (2)
H–I	127·0 (2), 118·2 (2)	125·1 (2), 122·1 (2)
H–K	114·6 (2), 116·0 (2)	116·0 (1), 116·4 (1)
I–J	133·7 (2), 123·8 (2)	130·1 (2), 126·5 (2)
I–K	118·3 (2), 125·6 (2)	118·9 (2), 121·5 (2)
J–J'	122·5 (2), —	128·3 (2), —
J–C(7)–O		116·1 (2), 115·6 (2)
K–L	122·4 (2), 119·4 (2),	121·1 (2), 120·7 (2),
	121·9 (2), 121·1 (2)	122·3 (2), 120·0 (2)
L–M	121·1 (2), 120·9 (2),	120·7 (2), 121·3 (2),
	120·0 (3), 122·5 (2)	121·3 (2), 120·7 (2)
L–L'	118·1 (2), —,	118·2 (2), —,
	116·8 (2), —	117·6 (2), —
M–N	120·0 (3), 119·6 (3),	120·8 (3), 119·1 (2),
	121·6 (3), 119·9 (3)	120·1 (2), 120·5 (2)
N–N'	120·3 (3), —	119·9 (3), —
	119·2 (3), —	119·7 (3), —

The torsion angles in the nine-membered rings, together with the internal C–C–C angles, show that NONCO is somewhat more symmetrical than NONCH$_2$. This situation presumably arises from the geometrical constraints imposed by the trigonal hybridization at C(7) in the ketone. Despite these differences, the overall planarities of the two central rings are virtually identical, with average deviations of the nine C atoms from their least-squares planes of

0·547 (5) and 0·549 (5) Å in NONCO and $NONCH_2$, respectively.

There are appreciable distortions in the $C_6H_5{-}C{=}C{-}X{-}C{=}C{-}C_6H_5$ fragments of the molecules, limiting π-electron interactions. The $C_6H_5{-}C{=}C$ torsion angles range from 11·3 (4), 40·2 (3)° in $NONCH_2$ to 25·6 (2), 29·2 (2)° in NONCO. The C=C's are approximately planar in both molecules. There is substantial distortion in the C=C–C=O fragments in NONCO, the central C–C bonds being twisted by 29·7 (3) and 55·0 (2)°. The torsional angles in these molecules suggests that conjugation between a substituent linked *via* the exocyclic double bond, and the π electrons in the nine-membered rings, will be minimal. Additionally, the π-electron system in the biphenyl fragment is effectively isolated by the large torsion angles (64–79°) in the bonds connecting this fragment to the $C_6H_5{-}C{=}C{-}X{-}C{=}C{-}C_6H_5$ region. It would seem that the double benzene annelation has stabilized the basic cyclononatetraene structure by effectively removing two of the C=C's from the ring, thereby converting it to a C=C–X–C=C structure. An example of the instability of the (I*a*) type of structure may be found in nonafulvene (I*a*, $X = CH_2$), which has a half-life of only 60 min in hexane solution at room temperature (Neuenschwander & Frey, 1975).

The crystal packing is ordinary.

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Structures of (*E*,*E*)-2,3-Butanedione Bis(4′-nitrophenylhydrazone) (I), $C_{16}H_{16}N_6O_4$, as the Bis(*N*,*N*-dimethylformamide) Adduct (III), $C_{16}H_{16}N_6O_4.2C_3H_7NO$, and (*E*)-2,3-Butanedione 4′-Nitrophenylhydrazone (II), $C_{10}H_{11}N_3O_3$

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Abstract. (III): $M_r = 502{\cdot}2$, $P\bar{1}$, $a = 11{\cdot}656\ (8)$, $b = 6{\cdot}888\ (6)$, $c = 8{\cdot}574\ (7)$ Å, $\alpha = 85{\cdot}4\ (1)$, $\beta = 69{\cdot}3\ (1)$, $\gamma = 94{\cdot}4\ (1)°$, $V = 637{\cdot}6$ Å^3, $Z = 1$, $D_m = 1{\cdot}31\ (1)$, $D_x = 1{\cdot}31$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}05$ cm^{-1}, $F(000) = 266$, $T = 298$ K, $R = 0{\cdot}086$ for 707 independent reflections. The molecule takes up the *E*,*E* conformation and contains a crystallographic centre of symmetry. There is a strong intermolecular hydrogen bond between each solvent *N*,*N*-dimethylformamide molecule and an NH group. (II): $M_r = 221{\cdot}1$, $P2_1/c$, $a = 12{\cdot}474\ (8)$, $b = 9{\cdot}220\ (7)$, $c = 10{\cdot}049\ (7)$ Å, $\beta = 112{\cdot}1\ (1)°$, $V = 1070{\cdot}6$ Å^3, $Z = 4$, $D_m = 1{\cdot}37\ (1)$ g cm^{-3}, $D_x = 1{\cdot}37$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}05$ cm^{-1}, $F(000) = 464$, $T = 298$ K, $R = 0{\cdot}066$ for 1023 independent reflections. Unusually for such molecules there is no intramolecular hydrogen bonding between the NH group and the carbonyl oxygen as has consistently been the case in all previously related structures. Instead there is an infinite chain of intermolecular hydrogen bonds.

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