X-ray Crystal Structure of *cyclo*-Tetrakis(*m*-phenylenesulfide)*

By Il'yas A. Zamaev, Valeri E. Shklover,† Yuri E. Ovchinnikov, Yuri T. Struchkov, Alexander V. Astankov, Vladimir I. Nedel'kin and Vladimir A. Sergeyev

AN Nesmeyanov Institute of Organoelement Compounds, USSR Academy of Sciences, 28 Vavilov St, Moscow B-334, USSR
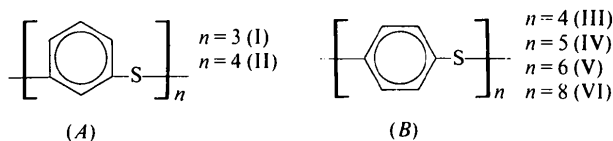
Abstract. 2,8,14,20-Tetrathiapentacyclo[19.3.1.1^{3,7}.-1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,-19(26),21,23-dodecaene, $C_{24}H_{16}S_4$, $M_r = 432.6$, triclinic, $P\bar{1}$, $a = 8.861$ (1), $b = 10.220$ (1), $c = 12.803$ (1) Å, $\alpha = 101.69$ (1), $\beta = 101.88$ (1), $\gamma = 105.69$ (1)°, $V = 1050.5$ (1) Å^3, $Z = 2$, $D_x = 1.368$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 4.5$ cm^{-1}, $F(000) = 448$, $T = 293$ K, $R = 0.051$ for 1927 reflections. Four S atoms of the macroheterocycle form a significantly flattened tetrahedron; the two benzene rings arranged opposite each other are approximately parallel to the mean plane of the four S atoms, while the other two benzene rings are approximately perpendicular to this plane. The S—C bond lengths in the two planar *cisoid* C—S—C—C moieties are somewhat shortened [1.757 and 1.758 (5) Å] in comparison with the other S—C bond lengths in the S—C macroheterocycle [1.773–1.799 (5) Å]. The C—S—C bond angles are 103.7–105.0 (2)°.

Introduction. In continuation of our study of the structures of oligomer precursors of organic or organoelement polymers we have carried out an X-ray structural study of *cyclo*-tetrakis(*m*-phenylenesulfide) (II). Previously we have determined the structures of other oligomers (I), (III), (V), (VI) in this series (Sergeyev, Ovchinnikov, Nedel'kin, Astankov, Andrianova, Shklover, Zamaev & Struchkov, 1988; Zamaev, Razumovskaya, Shklover, Struchkov, Astankov, Nedel'kin, Sergeyev & Ovchinnikov, 1989; Zamaev, Shklover, Struchkov, Astankov, Nedel'kin & Sergeyev, 1989a; Zamaev, Shklover, Struchkov, Astankov, Nedel'kin & Sergeyev, 1989b); the structural data for (IV) were reported earlier (Kaplan, Reents & Day, 1982).

In the case of *cyclo*-(*m*-phenylenesulfide)s (*A*) and *cyclo*-(*p*-phenylenesulfide)s (*B*) with small rings (*n* = 3, 4) the main problem lies in the determination of

their precise geometry (as potential ligands in the formation of complexes) and their possible steric hindrance, whereas the aim of an X-ray study of larger rings [of the (*B*) series with *n* = 6, 8] is to determine, along with the conformational characteristics, the crystal structural features including the topology of the internal cavities of the macrocycles which can incorporate small molecules, *e.g.* the molecules of solvents.

n = 3 (I)
n = 4 (II)

n = 4 (III)
n = 5 (IV)
n = 6 (V)
n = 8 (VI)

(*A*) (*B*)

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* B_{eq}($Å^2$) *in structure* (II)

$$B_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	$B_{eq/iso}$
S(1)	5430 (2)	2851 (2)	764 (1)	3·76 (5)
S(2)	−857 (2)	2210 (2)	1164 (1)	5·82 (7)
S(3)	2365 (2)	3632 (2)	5539 (1)	5·31 (6)
S(4)	7804 (2)	2220 (2)	4844 (1)	5·39 (7)
C(1)	3412 (5)	2895 (5)	351 (4)	3·0 (2)
C(2)	3102 (6)	3460 (6)	−535 (4)	4·6 (2)
C(3)	1580 (7)	3628 (6)	−877 (5)	5·4 (2)
C(4)	401 (6)	3232 (5)	−338 (4)	4·4 (2)
C(5)	720 (6)	2660 (5)	532 (4)	3·4 (2)
C(6)	2240 (6)	2495 (5)	882 (4)	3·1 (2)
C(7)	4 (6)	1675 (5)	2329 (4)	4·0 (2)
C(8)	−212 (7)	272 (5)	2265 (5)	5·4 (2)
C(9)	419 (8)	−99 (6)	3182 (5)	6·2 (3)
C(10)	1217 (6)	884 (5)	4181 (4)	4·6 (2)
C(11)	1444 (5)	2274 (5)	4245 (4)	3·8 (2)
C(12)	846 (6)	2719 (5)	3316 (4)	3·7 (2)
C(13)	4355 (6)	3524 (5)	5973 (4)	3·6 (2)
C(14)	5160 (7)	4089 (5)	7094 (4)	4·3 (2)
C(15)	6697 (7)	4067 (5)	7484 (4)	4·9 (2)
C(16)	7473 (6)	3476 (6)	6789 (4)	4·1 (2)
C(17)	6680 (6)	2907 (5)	5661 (4)	3·4 (2)
C(18)	5119 (6)	2940 (5)	5256 (4)	3·6 (2)
C(19)	6407 (6)	1488 (5)	3491 (4)	3·7 (2)
C(20)	5437 (7)	97 (6)	3139 (5)	5·1 (2)
C(21)	4447 (7)	−444 (5)	2059 (5)	6·0 (3)
C(22)	4396 (6)	363 (5)	1340 (5)	4·2 (2)
C(23)	5343 (5)	1764 (5)	1688 (4)	2·9 (2)
C(24)	6361 (5)	2353 (5)	2774 (4)	3·3 (2)

Discussion. The atomic positional and thermal parameters are given in Table 1.* The geometry of molecule (II) is shown in Fig. 1 where it is compared with the geometry of its isomer (p-C_6H_4S)$_4$ (III). Fig. 2 represents the side projection of molecule (II) illustrating most clearly the macroheterocycle conformation. Bond lengths and bond angles of molecule (II) are given in Table 2.

Just as in molecule (III) four S atoms S(1), S(2), S(3), S(4) of molecule (II) form a strongly flattened tetrahedron, the displacements of these atoms from their mean plane being −0·488 (2), 0·490 (2), −0·489 (2) and 0·488 (2) Å respectively. Triangles S(1)S(2)S(3) and S(1)S(4)S(3) form a dihedral angle of 27·0 (4)° which is somewhat larger than in the case of molecule (III) where the tetrahedron S_4 is bent by 16·0° and the displacement of the S atoms from their mean plane (plane A) are −0·279 (1), 0·329 (1), −0·305 (1) and 0·340 (1) Å.

The planes of the benzene rings B, C, D and E, form dihedral angles of 30·0 (1), 99·2 (2), 22·3 (1) and 79·6 (1)°, respectively, with the A plane of the four S atoms. The C and E benzene rings which are almost perpendicular to the A ring are almost paral-

* Tables of structure factors, anisotropic thermal parameters, H-atom coordinates and bond lengths and bond angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51904 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

lel to each other and form a dihedral angle of 19·6 (2)°, while the angle between the planes of the rings B and D turned towards the outside of the macroheterocycle is 130·0 (2)°. Quite noteworthy is a close approach of the planes of the C and E benzene rings, which can be seen in Fig. 1(a): the S(2) and S(3) atoms are displaced from the plane C by 0·089 (2) and 0·139 (2) Å towards the outside of the
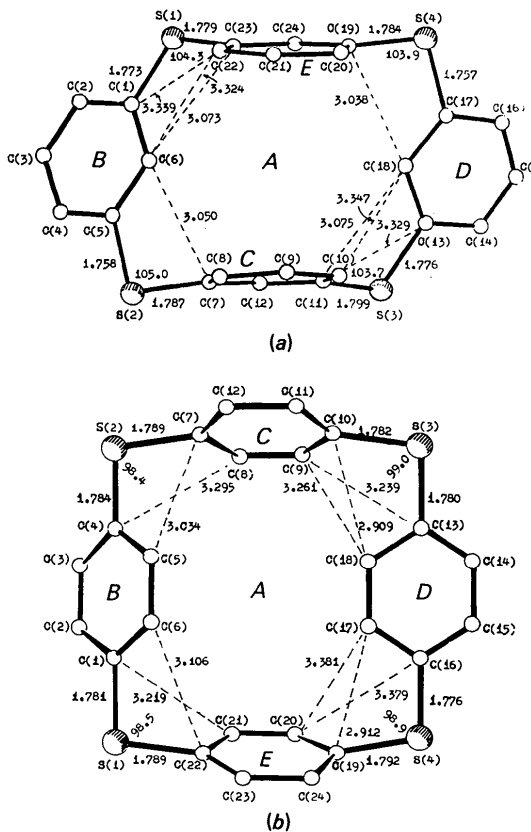

(a)

(b)

Fig. 1. Structures of the isomers: (a) (m-C_6H_4S)$_4$ (II) and (b) (p-C_6H_4S)$_4$ (III). Projections on the mean planes of the molecules are shown; the shortened non-bonded contacts (Å) are given. The e.s.d.s' are 0·005 Å (II), 0·003 Å (III) for the S—C bonds; 0·008Å (II) and 0·005Å (III) for the C—C bonds and 0·02° (II) and 0·01° (III) for the C—S—C bond angles.
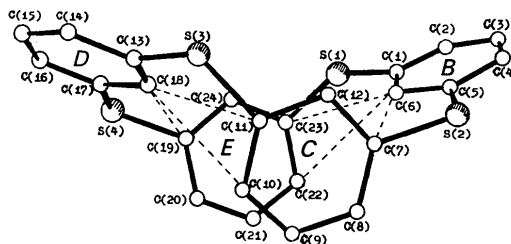

Fig. 2. Conformation of the macroheterocycle (II) [projection on the plane passing through atoms C(3), C(6), C(18) and C(15) and perpendicular to the mean plane of the molecule]. The non-bonded contacts determining the conformation are shown.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and endomacrocyclic torsion angles* (°) *in molecule* (II)

S(1)—C(1)	1·773 (5)	C(8)—C(9)	1·363 (8)
S(1)—C(23)	1·779 (5)	C(9)—C(10)	1·367 (8)
S(2)—C(5)	1·758 (5)	C(10)—C(11)	1·363 (8)
S(2)—C(7)	1·787 (5)	C(11)—C(12)	1·412 (7)
S(3)—C(11)	1·799 (5)	C(13)—C(14)	1·386 (7)
S(3)—C(13)	1·776 (6)	C(13)—C(18)	1·382 (7)
S(4)—C(17)	1·757 (5)	C(14)—C(15)	1·359 (8)
S(4)—C(19)	1·784 (5)	C(15)—C(16)	1·373 (8)
C(1)—C(2)	1·385 (7)	C(16)—C(17)	1·392 (7)
C(1)—C(6)	1·371 (7)	C(17)—C(18)	1·385 (7)
C(2)—C(3)	1·397 (9)	C(19)—C(20)	1·372 (8)
C(3)—C)4	1·383 (8)	C(19)—C(24)	1·399 (7)
C(4)—C)5	1·373 (7)	C(20)—C(21)	1·384 (8)
C(5)—C(6)	1·395 (7)	C(21)—C(22)	1·356 (8)
C(7)—C(8)	1·378 (8)	C(22)—C(23)	1·375 (7)
C(7)—C(12)	1·388 (7)	C(23)—C(24)	1·400 (7)

C(1)—S(1)—C(23)	104·3 (2)	C(10)—C(11)—C(12)	121·9 (5)
C(5)—S(2)—C(7)	105·0 (2)	C(7)—C(12)—C(11)	117·0 (5)
C(11)—S(3)—C(13)	103·7 (2)	S(3)—C(13)—C(14)	116·6 (4)
C(17)—S(4)—C(19)	103·9 (2)	S(3)—C(13)—C(18)	123·5 (4)
S(1)—C(1)—C(2)	114·6 (4)	C(14)—C(13)—C(18)	119·8 (5)
S(1)—C(1)—C(6)	124·6 (4)	C(13)—C(14)—C(15)	119·9 (5)
C(2)—C(1)—C(6)	120·6 (5)	C(14)—C(15)—C(16)	121·2 (5)
C(1)—C(2)—C(3)	119·1 (5)	C(15)—C(16)—C(17)	119·4 (5)
C(2)—C(3)—C(4)	120·4 (5)	S(4)—C(17)—C(16)	115·6 (4)
C(3)—C(4)—C(5)	119·9 (5)	S(4)—C(17)—C(18)	124·7 (4)
S(2)—C(5)—C(4)	116·1 (4)	C(16)—C(17)—C(18)	119·6 (5)
S(2)—C(5)—C(6)	123·8 (4)	C(13)—C(18)—C(17)	120·0 (5)
C(4)—C(5)—C(6)	120·1 (5)	S(4)—C(19)—C(20)	121·2 (4)
C(1)—C(6)—C(5)	120·0 (5)	S(4)—C(19)—C(24)	118·5 (4)
S(2)—C(7)—C(8)	121·3 (4)	C(20)—C(19)—C(24)	120·2 (5)
S(2)—C(7)—C(12)	117·6 (4)	C(19)—C(20)—C(21)	119·1 (5)
C(8)—C(7)—C(12)	121·0 (5)	C(20)—C(21)—C(22)	122·0 (6)
C(7)—C(8)—C(9)	119·6 (5)	C(21)—C(22)—C(23)	119·5 (5)
C(8)—C(9)—C(10)	121·7 (6)	S(1)—C(23)—C(22)	121·7 (4)
C(9)—C(10)—C(11)	118·8 (5)	S(1)—C(23)—C(24)	117·8 (4)
S(3)—C(11)—C(10)	122·0 (4)	C(22)—C(23)—C(24)	120·3 (5)
S(3)—C(11)—C(12)	115·9 (4)	C(19)—C(24)—C(23)	118·8 (5)

C(23)—S(1)—C(1)—C(6)	15·6 (4)	C(11)—S(3)—C(13)—C(18)	22·3 (4)
C(6)—C(5)—S(2)—C(7)	4·2 (4)	C(18)—C(17)—S(4)—C(19)	−5·1 (4)
C(5)—S(2)—C(7)—C(12)	86·6 (4)	C(17)—S(4)—C(19)—C(24)	90·2 (4)
C(12)—C(11)—S(3)—C(13)	−123·3 (4)	C(24)—C(23)—S(1)—C(1)	−120·9 (4)

macroheterocycle, while the S(1) and S(4) atoms are displaced from the E plane by 0·114 (2) and 0·109 (2) Å respectively. The mean distance of the atoms of the E ring from the C plane is 4·59 Å.

As in molecule (III), the conformation of the macroheterocycle in molecule (II) is determined by the non-bonded contacts C···C (Figs. 1 and 2). Despite the fact that the S···S distances between the nearest S atoms in (II) are smaller than in (III) [5·433–5·577 (2) and 6·281–6·356 (1) Å respectively] the number of short C···C distances in (II) is less than in (III) (eight and ten contacts respectively). Steric hindrance in (II) is decreased due to the outward twisting of the two benzene rings (Fig. 2).

The conformation of the 16-membered heterocycle is described by the eight torsion angles C—S—C—C (Table 2), as the eight endocyclic torsion angles of the S—C—C—C type are constrained to be close to 180°. The absolute values of the torsion angles C—S—C—C around the S—C bonds at the benzene

rings B and D do not exceed 23° while the corresponding values for the C and E rings are 87–123°. As a result the C(7) and C(23), C(11) and C(19), C(5) and C(13), C(1) and C(17) atoms are displaced from the planes B, D, C and E by 0·173 (5) and −0·248 (5), 0·619 (5) and 0·085 (5), 1·581 (5) and 1·296 (5), 1·354 (5) and 1·569 (5) Å respectively.

In the previously studied macrocycles (I) and (III)–(VI) all S—C distances are quite close: 1·767–1·786 (4) Å (av. 1·780 Å) in (I), 1·776–1·792 (3) Å (av. 1·784 Å) in (III), 1·771–1·784 (4) Å (av. 1·778 Å) in (IV), 1·771–1·788 Å (av. 1·779 Å) in (V) and 1·773–1·791 (8) Å (av. 1·781 Å) in (VI). On the contrary, in molecule (II) a pronounced shortening of the S—C bonds in the approximately planar *cisoid* fragments C—S—C—C (Table 2) is observed. The S(2)—C(5) and S(4)—C(17) distances are shortened to 1·758 (5) and 1·757 (5) Å respectively. All other S—C bond lengths in molecule (II) [1·773–1·799 (5) Å, av. 1·783 Å] are close to those observed in (I)–(VI).

In the B series, on passing from the oligomers $\overline{(C_6H_4S)_n}$ with $n = 5$, 6 and 8 [(IV)–(VI)] to the sterically hindered tetramer (III), the bond angles C—S—C decrease abruptly [101·9–103·0 (2), av. 102·5° in (IV); 100·1–104·0 (2), av. 102·5° in (V); 101·7–105·6 (4), av. 103·6° in (VI); 98·4–99·0 (1), av. 98·7° in (III)]. The compounds of the m-series A have been studied to a lesser extent. A certain variation of the bond angles C—S—C [98·4–104·5 (4), av. 101·7°] is observed in (I). In (II) the bond angles C—S—C vary in a narrow interval of 103·7–104·9 (2)° (av. 104·2°), which is close to the upper limit for the C—S—C angles in the strained oligomers of the B series. This feature is likely to explain the above-mentioned close approach of the benzene rings C and E as it prevents too large a widening of the bond angles C—S—C in the molecule (II).
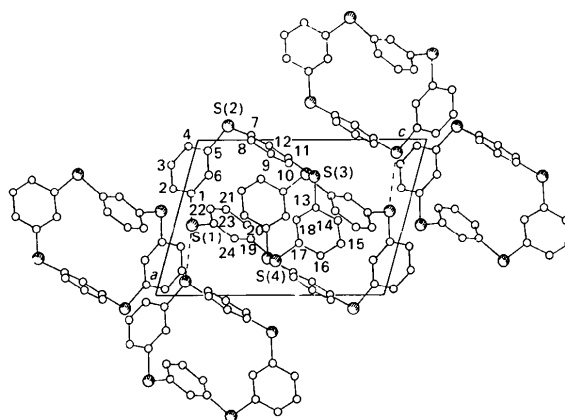

Fig. 3. The molecular packing in crystal (II). The short intermolecular distances S(1)···S(2) ($x + 1$, y, z) are shown by broken lines.

In the crystal (II) the intermolecular $S(1)\cdots S(2)$ distance between the molecules related by a translation of 3·482 (2) Å is shorter than the doubled van der Waals radius of the S atom 3·60 Å (Bondi, 1964). In the same direction of crystal (II) there are a number of distances close to the corresponding sums of the van der Waals radii: $S(3)\cdots S(4)$ 3·749 (2), $S(2)\cdots C(23)$ 3·495 (5), $S(2)\cdots C(24)$ 3·536 (5), $S(4)\cdots C(11)$ 3·455 and $S(4)\cdots C(12)$ 3·631 (5) Å (the van der Waals radii sum of the S and C atoms is 3·50 Å; Bondi, 1964). The molecular packing for (II) is shown in Fig. 3.

References

BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.

GERR, R. G., YANOVSKY, A. I. & STRUCHKOV, YU. T. (1983). *Kristallografiya,* **28**, 1029–1031.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
KAPLAN, M. L., REENTS, W. D. & DAY, C. S. (1982). *Cryst. Struct. Commun.* 11, 1751–1758.
SERGEYEV, V. A., OVCHINNIKOV, YU. E., NEDEL'KIN, V. I., ASTANKOV, A. V., ANDRIANOVA, O. B., SHKLOVER, V. E., ZAMAEV, I. A. & STRUCHKOV, YU. T. (1988). *Izv. Akad. Nauk SSSR Ser. Khim.* pp. 1625–1629.
ZAMAEV, I. A., RAZUMOVSKAYA, I. V., SHKLOVER, V. E., STRUCHKOV, YU. T., ASTANKOV, A. V., NEDEL'KIN, V. I., SERGEYEV, V. A. & OVCHINNIKOV, YU. E. (1989). *Acta Cryst.* C45, 121–123.
ZAMAEV, I. A., SHKLOVER, V. E., STRUCHKOV, YU. T., ASTANKOV, A. V., NEDEL'KIN, V. I. & SERGEYEV, V. A. (1989a). *Zh. Strukt. Khim.* In the press.
ZAMAEV, I. A., SHKLOVER, V. E., STRUCHKOV, YU. T., ASTANKOV, A. V., NEDEL'KIN, V. I. & SERGEYEV, V. A. (1989b). *Zh. Strukt. Khim.* In the press.

Conformation of Cyclic Alkoxy Indanones and Indanonols

BY S. IANELLI AND M. NARDELLI*

Istituto di Chimica Generale, Università degli Studi di Parma, Centro di Studio CNR per la Strutturistica Diffrattometrica, Viale delle Scienze, I-43100 Parma, Italy

D. BELLETTI

Istituto di Strutturistica Chimica, Università degli Studi di Parma, Centro di Studio CNR per la Strutturistica Diffrattometrica, Viale delle Scienze, I-43100 Parma, Italy

AND B. JAMART-GRÉGOIRE, M. C. CARRÉ AND P. CAUBÈRE

Laboratoire de Chimie Organique I, UA CNRS No. 457, Université de Nancy I, BP 239, 54506 Vandoeuvre-Les-Nancy CEDEX, France

Abstract. The crystal structures of the following cyclo alkoxy indanone and indanonols, obtained by transposition of benzocyclobutenols in the presence of acids, the first under aprotic, the rest under protic conditions, have been determined using Cu $K\alpha_1$ ($\lambda = 1.540562$ Å) at room temperature [293 (2) K]. Crystal data are as follows: 2-hydroxy-2,3-hexamethyleneindan-1-one (IV,5), $C_{15}H_{18}O_2$, $M_r = 230.3$, monoclinic, $P2_1/c$, $a = 10.693$ (1), $b = 14.144$ (1), $c = 9.320$ (1) Å, $\beta = 115.92$ (1)°, $V = 1267.8$ (2) Å^3, $Z = 4$, $D_x = 1.207$ Mg m^{-3}, $\mu = 0.587$ mm^{-1}, $F(000) = 496$, $R = 0.0444$ for 1724 observed reflections; 2-hydroxy-2,3-octamethyleneindan-1-one (IV,7), $C_{17}H_{22}O_2$, $M_r = 258.4$, monoclinic, $P2_1/n$, $a = $ 21·752 (6), $b = 9.377$ (2), $c = 14.779$ (4) Å, $\beta = 105.41$ (3)°, $V = 2906$ (1) Å^3, $Z = 8$, $D_x = 1.181$ Mg m^{-3}, $\mu = 0.559$ mm^{-1}, $F(000) = 1120$, $R = 0.0516$ for 2481 observed reflections; 2-methoxy-2,3-nonamethyleneindan-1-one (V,8), $C_{19}H_{26}O_2$, $M_r = 286.4$, monoclinic, $P2_1/a$, $a = 7.552$ (1), $b = 19.993$ (9), $c = 11.401$ (3) Å, $\beta = 109.13$ (1)°, $V = 1626.3$ (9) Å^3, $Z = 4$, $D_x = 1.170$ Mg m^{-3}, $\mu = 0.542$ mm^{-1}, $F(000) = 624$, $R = 0.0413$ for 1794 observed reflections. The stereochemistry at the junctions of the polymethylene rings with the penta-atomic ring of indanone is *cis* for (IV,5) and (V,8), *trans* for (IV,7). The conformations of the puckered polymethylenic rings show relevant differences with respect to the calculated minimum-energy conformations of the corresponding unsubstituted cyclo-

* To whom all correspondence should be addressed.