be a minimum, hence defining a least-motion reaction path. The r.m.s. displacement for MSHD is also large so that it does not provide a critical test of the criteria. The crystal structure data for other diacetylenes suggests, however, that the simple criterion of Schmidt is adequate for the assessment of solid-state reactivity of diacetylenes.

The larger monomer separation for MSHD relative to TSHD and BSHD [5·774 (2) compared with 5·159 (1) and 5·280 (1) Å] is due to the presence of the larger number of bulky methyl groups.

This work was supported by grants from the SERC.

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*Acta Cryst.* (1985). C**41**, 229–232

# The Structure of the 2/1 'Channel' Inclusion Compound between Deoxycholic Acid and Pinacolone, $2C_{24}H_{40}O_4.C_6H_{12}O$

BY V. M. COIRO, F. MAZZA AND G. POCHETTI

*Istituto di Strutturistica Chimica 'G. Giacomello', CNR, CP no.* 10, 00016 *Monterotondo Stazione, Roma, Italy*

AND E. GIGLIO AND N. V. PAVEL

*Dipartimento di Chimica, Università di Roma, P.le A. Moro* 5, 00185 *Roma, Italy*

(*Received* 6 *March* 1984; *accepted* 26 *September* 1984)

**Abstract.** $M_r = 885·32$, orthorhombic, $P2_12_12_1$, $a = 27·132\ (7)$, $b = 13·543\ (2)$, $c = 14·228\ (2)$ Å, $V = 5228\ (2)$ Å$^3$, $Z = 4$, $D_x = 1·12$ Mg m$^{-3}$, Cu $K\alpha$, $\lambda = 1·5418$ Å, $\mu = 0·6$ mm$^{-1}$, $F(000) = 1952$, room temperature, $R = 0·078$ and $R_w = 0·079$ for 3067 independent reflections with $I > 1·5\ \sigma(I)$. The crystal packing is very similar to those found in the deoxycholic acid inclusion compounds with norbornadiene and quadricyclane (tetracyclo[2.2.1.0$^{2,6}$.0$^{3,5}$]heptane), and is characterized by an assembly of antiparallel pleated bilayers of the steroid molecules, which pack together leaving empty spaces occupied by the guest molecules. The cross section of the channels is almost square. The centers of gravity of pinacolone, which assumes in the channels two different orientations related by a pseudo twofold axis, have coordinates approximately equal to those of norbornadiene and quadricyclane.

**Introduction.** The reversible valence isomerization of norbornadiene (NBD) to quadricyclane (QDC) is an attractive process for the chemical storage of solar energy (Hautala, Little & Sweet, 1977). Because of the lack of overlap between the electronic absorption spectrum of NBD and the solar radiance spectrum, the direct conversion NBD→QDC by sunlight is precluded. However, this conversion is still achievable by means of photosensitizers. Since the quantum efficiency of the reaction and the purity of QDC could be improved inside the channels of an inclusion compound, those of the deoxycholic acid (DCA) were chosen for this purpose.

The inclusion compounds between DCA and NBD (DCANBD; D'Andrea, Fedeli, Giglio, Mazza & Pavel, 1981) and QDC (DCAQDC; Coiro, Giglio, Mazza & Pavel, 1984) were studied in order to establish whether the DCA host lattices are nearly equal. Since the DCA host lattice does not change, it is possible to foresee that it can easily tolerate the lattice-controlled photoinduced reaction NBD→QDC, without destroying the crystal structure of the inclusion compound. Furthermore, the structural information gained from the crystal packing of DCANBD and DCAQDC is useful for the choice of

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a photosensitizer with steric requirements suitable for its inclusion, together with NBD, in the DCA channels. Among different photosensitizers one of the most promising appeared to be pinacolone (PNC) and, therefore, the inclusion compound between DCA and PNC (DCAPNC) was prepared.

**Experimental.** Single crystals of DCAPNC obtained by slow evaporation of methanol solution of two components in 2:1 molar ratio. Host–guest ratio determined by $^1$H NMR spectra of crystals dissolved in $(CD_3)_2SO$. Crystal $0·3 \times 0·2 \times 0·1$ mm, automatic Syntex $P2_1$ diffractometer, graphite monochromator. Unit-cell parameters refined by least-squares fit of angular settings of 15 reflections, $10 < \theta < 35°$. Intensities to max. $2\theta$ of 110°, $\theta$–$2\theta$ scan. Three reflections, 230, 802 and 040, measured after every 97, showed small deviations from means. 3742 independent reflections, 3070 with $I > 1·5\,\sigma(I)$ considered observed and used for calculations. $h$ 0–26, $k$ 0–14, $l$ 0–14. Lorentz and polarization corrections, no corrections for extinction and absorption. Structure solved by assuming for DCA atomic coordinates for DCANBD. Subsequent structure factors and Fourier synthesis calculations without PNC allowed $R$ to decrease to 0·20. Difference Fourier synthesis showed most atoms of PNC. However, owing to the low contribution of atoms of PNC to structure factors (except $hk0$), PNC was treated as rigid body in refinement. Model assumed for PNC is characterized by following values: 1·54 Å for all C—C bond lengths, 1·23 Å for C=O carbonyl bond, 109·5° for all valence angles involving C $sp^3$ atoms, 121° for O—C—C angles and 118° for valence angle opposite carbonyl group. Starting position of model obtained by applying a 'molecule best fitting' program to peaks of the Fourier difference synthesis. Full-matrix least-squares refinement with *SHELX* (Sheldrick, 1976), $w = k_1/[\sigma^2(F_o) + k_2F_o^2]$, $k_1$ and $k_2$ redetermined after each cycle. Function minimized $\sum w(|F_o|-|F_c|)^2$. Atoms of PNC refined isotropically, those of DCA molecules anisotropically, fixing in each cycle thermal parameters of one of the two DCA molecules alternately, since *SHELX* does not allow anisotropic refinement of all 56 DCA heavy atoms. Hydrogen atoms of DCA, except those of hydroxyl and carboxyl groups, generated after each cycle at expected positions, with thermal parameters approximately equal to those of carrier atoms. Refinement converged to $R$ and $R_w$ of 0·088 and 0·091, respectively. Difference Fourier synthesis showed residual electronic density among methyls of *tert*-butyl group, which was interpreted as due to a second orientation of guest molecule, related to the first by a pseudo twofold axis parallel to **c**. The differently oriented PNC molecules were refined isotropically as two independent rigid bodies, assuming an occupancy factor of 0·5 for the atoms of each, together with the two DCA molecules; the anisotropic thermal parameters of C(8), C(9) and C(14) of the first DCA molecule and correspondingly those of C(36), C(37) and C(42) of the second DCA molecule were held fixed in the refinement. Three reflections, 110, 102 and 400, excluded because of probable influence by extinction. Final $R$ and $R_w$ 0·078 and 0·079. Thermal values of both PNC molecules and all e.s.d.'s decreased significantly with respect to single oriented PNC refinement. The final two orientations of PNC are shown overlapped in Fig. 1. Final values of $k_1$ and $k_2$ in weighting function 11·7478 and 0·0002, respectively. Max. and min. height in final Fourier difference synthesis 0·3 and −0·3 e Å$^{-3}$, $(\Delta/\sigma)_{max} = 0·097$ for the two DCA molecules (0·492 for the two PNC molecules). Atomic scattering factors those of Cromer & Mann (1968).

**Discussion.** The final atomic parameters of the non-H atoms are reported in Table 1,* while Fig. 2 shows the numbering scheme adopted for the DCA molecules together with the bond lengths and angles involving non-H atoms. The geometry and the conformation of both side chain and $D$ ring of the two DCA molecules are comparable to each other and to those of the other orthorhombic and tetragonal crystals (Coiro, Giglio, Mazza, Pavel & Pochetti, 1982; Coiro, D'Andrea & Giglio, 1979). The conformation of the side chain is *gauche* and the $D$ ring approaches half-chair symmetry (Giglio & Quagliata, 1975). The torsion angles are listed in Table 2, according to the convention of Klyne & Prelog (1960), together with the phase angle of pseudorotation $\Delta$ and the maximum angle of torsion $\varphi_m$ (Altona, Geise & Romers, 1968). The crystal packing is characterized by an assembly of antiparallel pleated bilayers, formed by molecules of DCA held together through hydrogen bonds, which extend into the $bc$ plane, and is practically the same as those found in the crystals of DCANBD and DCAQDC. The hydrogen

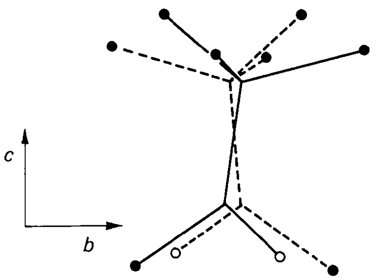

Fig. 1. The final positions of PNC in the two orientations, represented by full and dashed lines. The view is along **a**.

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* Lists of structure factors and anisotropic thermal parameters have been been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39783 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bonds are described in Table 3. The guest molecules fill the non-polar channels with cross section about 4·9 × 5·4 Å.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and thermal parameters* ($\text{Å}^2 \times 10^3$) *for the non*-H *atoms of DCAPNC with their e.s.d.'s in parentheses*

$$U_{\text{eq}} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

| | $x$ | $y$ | $z$ | $U_{\text{eq}}/U$ |
|---|---|---|---|---|
| C(1) | 1120 (3) | 1790 (5) | −764 (5) | 58 (2) |
| C(2) | 617 (3) | 2128 (5) | −418 (5) | 62 (2) |
| C(3) | 687 (3) | 2857 (5) | 394 (5) | 63 (2) |
| C(4) | 978 (3) | 2413 (5) | 1181 (5) | 64 (2) |
| C(5) | 1488 (3) | 2025 (5) | 839 (5) | 59 (2) |
| C(6) | 1782 (3) | 1576 (5) | 1649 (5) | 64 (3) |
| C(7) | 1588 (3) | 573 (5) | 1968 (5) | 69 (3) |
| C(8) | 1533 (3) | −151 (5) | 1152 (4) | 53* |
| C(9) | 1212 (2) | 309 (5) | 360 (4) | 48* |
| C(10) | 1439 (2) | 1298 (5) | 1 (5) | 53 (2) |
| C(11) | 1101 (2) | −445 (5) | −412 (4) | 49 (2) |
| C(12) | 871 (2) | −1406 (5) | −45 (4) | 49 (2) |
| C(13) | 1197 (2) | −1877 (5) | 723 (4) | 50 (2) |
| C(14) | 1272 (3) | −1094 (5) | 1488 (4) | 52* |
| C(15) | 1514 (3) | −1676 (5) | 2292 (5) | 67 (3) |
| C(16) | 1258 (3) | −2687 (5) | 2240 (5) | 74 (3) |
| C(17) | 965 (3) | −2733 (5) | 1321 (5) | 59 (2) |
| C(18) | 1686 (2) | −2212 (5) | 263 (5) | 59 (2) |
| C(19) | 1950 (2) | 1117 (6) | −439 (5) | 63 (2) |
| C(20) | 960 (3) | −3781 (5) | 910 (5) | 59 (2) |
| C(21) | 678 (3) | −3873 (5) | −28 (5) | 70 (3) |
| C(22) | 772 (3) | −4552 (5) | 1645 (6) | 68 (3) |
| C(23) | 253 (3) | −4396 (5) | 1961 (6) | 85 (3) |
| C(24) | 86 (3) | −5197 (6) | 2641 (6) | 79 (3) |
| O(25) | 195 (2) | 3140 (4) | 717 (4) | 86 (2) |
| O(26) | 384 (2) | −1211 (3) | 316 (3) | 65 (2) |
| O(27) | 110 (3) | −6066 (4) | 2476 (4) | 125 (2) |
| O(28) | −72 (2) | −4873 (3) | 3446 (4) | 78 (2) |
| C(29) | 1186 (3) | 1851 (5) | 4322 (5) | 60 (2) |
| C(30) | 692 (3) | 2174 (5) | 4737 (5) | 65 (2) |
| C(31) | 775 (3) | 2891 (5) | 5552 (5) | 66 (3) |
| C(32) | 1103 (3) | 2446 (5) | 6292 (5) | 65 (2) |
| C(33) | 1600 (3) | 2082 (5) | 5885 (5) | 63 (2) |
| C(34) | 1928 (3) | 1622 (5) | 6640 (5) | 69 (3) |
| C(35) | 1754 (3) | 617 (5) | 6977 (5) | 68 (3) |
| C(36) | 1665 (3) | −95 (5) | 6171 (5) | 54* |
| C(37) | 1318 (2) | 365 (4) | 5429 (4) | 46* |
| C(38) | 1534 (2) | 1359 (5) | 5044 (5) | 52 (2) |
| C(39) | 1185 (2) | −388 (5) | 4659 (4) | 52 (2) |
| C(40) | 955 (2) | −1323 (5) | 5049 (5) | 50 (2) |
| C(41) | 1298 (2) | −1806 (5) | 5778 (5) | 53 (2) |
| C(42) | 1404 (3) | −1037 (5) | 6538 (5) | 56* |
| C(43) | 1676 (3) | −1640 (5) | 7303 (5) | 70 (3) |
| C(44) | 1396 (3) | −2626 (6) | 7303 (5) | 77 (3) |
| C(45) | 1076 (3) | −2659 (5) | 6411 (5) | 59 (2) |
| C(46) | 1771 (2) | −2172 (5) | 5278 (5) | 58 (2) |
| C(47) | 2030 (2) | 1185 (6) | 4540 (5) | 65 (2) |
| C(48) | 1050 (3) | −3700 (5) | 6004 (5) | 58 (2) |
| C(49) | 759 (3) | −3782 (5) | 5069 (5) | 69 (3) |
| C(50) | 850 (3) | −4459 (5) | 6745 (6) | 66 (3) |
| C(51) | 323 (3) | −4277 (5) | 7056 (6) | 79 (3) |
| C(52) | 129 (3) | −5096 (6) | 7697 (5) | 70 (3) |
| O(53) | 301 (2) | 3153 (4) | 5938 (4) | 87 (2) |
| O(54) | 484 (2) | −1119 (3) | 5460 (3) | 63 (2) |
| O(55) | 275 (3) | −5925 (4) | 7687 (4) | 119 (2) |
| O(56) | −184 (2) | −4774 (3) | 8305 (4) | 78 (2) |
| C(57) | 2234 (4) | 4120 (9) | 1927 (8) | 229 (3) |
| C(58) | 2545 (4) | 4917 (9) | 2422 (8) | 188 (3) |
| O(59) | 2853 (4) | 5401 (9) | 1986 (8) | 221 (3) |
| C(60) | 2459 (4) | 5088 (9) | 3479 (8) | 140 (3) |
| C(61) | 1919 (4) | 4850 (9) | 3723 (8) | 177 (3) |
| C(62) | 2569 (4) | 6175 (9) | 3721 (8) | 161 (3) |
| C(63) | 2803 (4) | 4412 (9) | 4050 (8) | 177 (3) |
| C(67) | 2666 (5) | 5869 (10) | 1866 (9) | 241 (3) |
| C(68) | 2398 (5) | 5057 (10) | 2424 (9) | 194 (3) |
| O(69) | 2107 (5) | 4493 (10) | 2036 (9) | 281 (3) |
| C(70) | 2505 (5) | 4972 (10) | 3484 (9) | 131 (3) |
| C(71) | 3036 (5) | 5318 (10) | 3682 (9) | 183 (3) |
| C(72) | 2447 (5) | 3889 (10) | 3795 (9) | 160 (3) |
| C(73) | 2140 (5) | 5623 (10) | 4035 (9) | 231 (3) |

* The anisotropic thermal parameters were held fixed in the last stages of refinement.

The two orientations, related by a pseudo twofold axis parallel to **c**, of PNC in the DCA channel are shown in Fig. 3. The van der Waals interactions between the host and guest molecules inside the channel are similar in the two cases, as shown in Table 4.

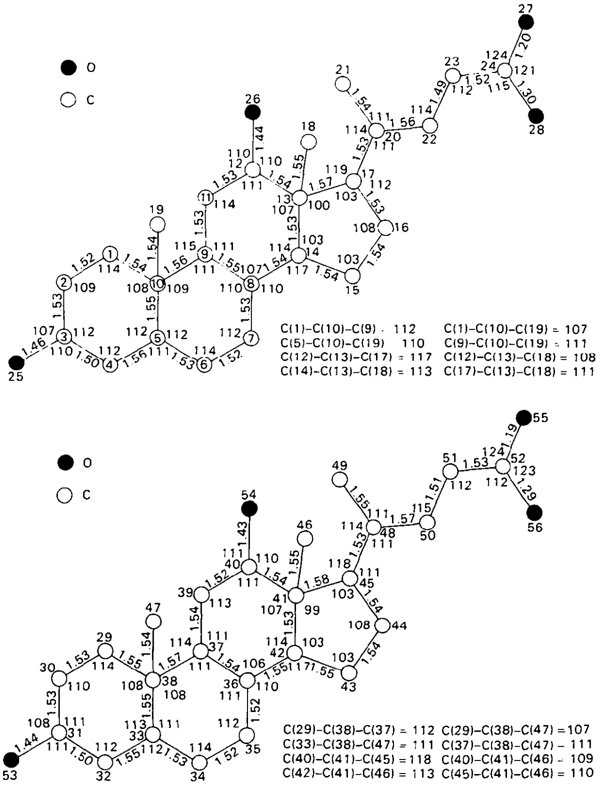

Fig. 2. Atomic numbering, bond distances (Å) and angles (°) for the two DCA molecules of the DCAPNC asymmetric unit. E.s.d.'s are in the ranges 0·008–0·012 Å and 0·4–0·8°, respectively, for bond lengths and angles.

Table 2. *Torsion angles* (°) *for the side chain and ring D of the two independent DCA molecules together with* $\Delta$ *and* $\varphi_m$

The e.s.d.'s are in the range 0·6–1·1° for the torsion angles.

| | Molecule C(1)–O(28) | Molecule C(29)–O(56) |
|---|---|---|
| C(13)–C(17)–C(20)–C(22) | 173 | 177 |
| C(17)–C(20)–C(22)–C(23) | 63 | 64 |
| C(20)–C(22)–C(23)–C(24) | 177 | 174 |
| C(13)–C(17)–C(20)–C(21) | −59 | −57 |
| C(16)–C(17)–C(20)–C(21) | −179 | −177 |
| C(21)–C(20)–C(22)–C(23) | −66 | −65 |
| C(22)–C(23)–C(24)–O(27) | −54 | −26 |
| C(22)–C(23)–C(24)–O(28) | 124 | 148 |

| | Molecule C(1)–O(28) | Molecule C(29)–O(56) |
|---|---|---|
| C(13)–C(14) | 47 | 48 |
| C(14)–C(15) | −36 | −39 |
| C(15)–C(16) | 11 | 14 |
| C(16)–C(17) | 18 | 15 |
| C(13)–C(17) | −39 | −39 |
| $\Delta$ | 8 | 1 |
| $\varphi_m$ | 47 | 48 |

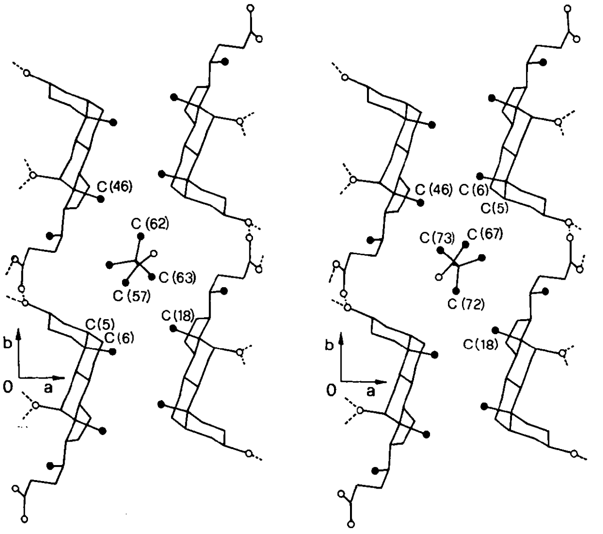

Fig. 3. DCAPNC channel viewed along **c**. Broken lines, filled and open circles represent hydrogen bonds, methyl groups and oxygen atoms, respectively. The two orientations of PNC in the DCA channel are shown. The atoms that interact as summarized in Table 4 are indicated.

The PNC molecule occupies approximately the same position of NBD and QDC in DCANBD and DCA-QDC crystals. The coordinates of the centers of gravity of PNC, considering only the non-H atoms, are (0·248, 0·499, 0·304) and (0·247, 0·503, 0·305), respectively, for the first and second PNC molecules quoted in Table 1, whereas those of NBD and QDC are (0·253, 0·505, 0·331) and (0·248, 0·505, 0·331) respectively. Therefore, since the host structures are nearly equal in DCANBD, DCAQDC and DCAPNC it should be possible to include NBD together with PNC in the channels of DCA. These guest molecules could exchange their positions in the same channel without straining the lattice, so that the lattice-controlled photoinduced reaction NBD→QDC could easily occur.

Table 3. O···O *distances* (Å) *of the hydrogen bonds in a bilayer*

E.s.d.'s are in the range 0·007–0·008 Å.

| | | | |
|---|---|---|---|
| $O(25)\cdots O(27^{i})$ | 2·73 | $O(26)\cdots O(53^{iii})$ | 2·72 |
| $O(25)\cdots O(54^{ii})$ | 2·69 | $O(53)\cdots O(55^{i})$ | 2·78 |
| $O(26)\cdots O(28^{ii})$ | 2·66 | $O(54)\cdots O(56^{iv})$ | 2·66 |

Symmetry code: (i) $x, 1+y, z$; (ii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iv) $-x, \frac{1}{2}+y, \frac{3}{2}-z$.

Table 4. *Shortest contacts* (Å) *between PNC and DCA atoms*

E.s.d.'s are in the range 0·013–0·015 Å for methyl–methyl distances.

The numbering of DCA hydrogens is that of the carrier carbons.

| | | | |
|---|---|---|---|
| $C(62)\cdots C(46^{i})$ | 3·82 | $C(72)\cdots C(18^{ii})$ | 3·88 |
| $C(63)\cdots C(18^{ii})$ | 3·71 | $C(73)\cdots C(46^{i})$ | 3·61 |
| $C(57)\cdots H(5)$ | 3·12 | $C(67)\cdots H(33^{iii})$ | 3·00 |
| $C(57)\cdots Ha(6)$ | 3·07 | $C(67)\cdots Ha(34^{iii})$ | 2·98 |

Symmetry code: (i) $x, 1+y, z$; (ii) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (iii) $\frac{1}{2}-x, 1-y, \frac{1}{2}-z$.

One of the authors (EG) acknowledges financial support from the Consiglio Nazionale delle Ricerche. Drawings by Mr M. Viola.

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*Acta Cryst.* (1985). C**41**, 232–234

# (1*RS*)-15-Thiabicyclo[10.7.0]nonadec-1(12)-ene 15,15-Dioxide, $C_{18}H_{32}O_2S$

BY S. K. RAMASESHA, S. F. WATKINS AND F. R. FRONCZEK

*Department of Chemistry, Louisiana State University, Baton Rouge, LA* 70803, *USA*

(*Received* 31 *May* 1984; *accepted* 27 *September* 1984)

**Abstract.** $M_r = 312·0$, triclinic, $P\bar{1}$, $a = 8·618$ (4), $b = 12·403$ (3), $c = 16·792$ (6) Å, $\alpha = 88·24$ (3), $\beta = 79·82$ (3), $\gamma = 87·29$ (3)°, $V = 1764$ (1) Å$^3$, $Z = 4$, $D_x = 1·18$ g cm$^{-3}$, Mo $K\alpha$, $\lambda = 0·71073$ Å, $\mu = 1·8$ cm$^{-1}$, $F(000) = 688$, $T = 295$ K, final $R = 0·067$ over 3033 reflections. Each molecule consists of a 5-thiacyclononene ring (*A*) *trans* fused to a cyclododecene ring (*B*). The flexibility of ring *B* results in

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