CONFORMATION OF CYCLOHEXANE RING IN SOME POLYCYCLIC MOLECULES

UDC 541.6:547.592.12

M. S. Salakhov, A. P. Timosheva,
S. G. Vul'fson, R. S. Salakhova,
N. É. Musaeva, N. A. Alekperov,
and A. N. Vereshchagin

A cyclohexane ring that contains two planar groupings in the 1,4 position exists in the conformation of a bathtub. The fixing of three bonds of the ring in one plane can be accomplished by condensation with a three-membered ring, a planar five-membered anhydride or imide ring [1, 2], or a bicyclic system [3, 4]. The conformation of molecules that contain three-membered rings is affected by certain specific factors, which are related to the difference in the hybridization of the carbon atoms that enter into these rings from the sp³ type. The spatial structure of the 1,4-diplanar six-membered rings with an sp³ hybridization of all of the atoms (cyclohexane ring) was discussed previously in [5], where the conformation of a bathtub was established for a cyclohexane ring, condensed with a bicyclic system and a five-membered anhydride ring, and a selection was made of one of the two possible structures on the basis of an examination of the models.

In order to obtain experimental confirmation of this assumption we used the method of dipole moments (DM) to study the spatial structure of a number of tetracyclic and pentacyclic compounds, which represented the adducts of the diene synthesis of hexachlorocyclopentadiene and its analogs with the anhydrides and imides of cis-4-cyclohexene-1,2-dicarboxylic acids (I)-(IX), and also some of their further transformation products (X)-(XI)



(I), (VII) and (X): X = 0, R = R' = H; (II), (III), (VIII) and (XI): X = 0, $R = CH_{2g} R' = H$; (IV), (V): X = 0, R = H, $R' = CH_{2g}$; (VI): $X = NC_6H_5$, R = R' = H; (IX): $X = NC_6H_5$, $R = CH_{2g} R' = H$

The configuration of the adducts of hexachlorocyclopentadiene and the corresponding ketones, obtained from the adducts of 5,5-dimethoxytetrachlorocyclopentadiene, is identical [5]. It is known that in (I) and (VII) the bicyclic system and the anhydride ring have a trans-orientation, i.e., they are located on different sides of the cyclohexane fragment [5]. In addition, analogous anhydrides and imides can be assigned to one conformation series [6]. As a result, for the nonmethylated tetracyclic derivatives (I), (VI), and (VII) the problem consists in determining the conformation of the six-membered ring. Since it has the shape of a bathtub with trans-coupled fragments, two spatial structures are possible, in which the bonds of the bicyclic system (Fig. 1A) or of the five-membered ring (Fig. 1B) occupy an equatorial position. In harmony with the orientation of the anhydride or imide rings relative to the bonds of the six-membered ring, they can be designated as syn A and anti B, which differ substantially in the mutual orientation of the polar bonds.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Branch, Academy of Sciences of the USSR. Yu. G. Mamedaliev Sumgaitskii Branch, Institute of Petrochemical Processes, Academy of Sciences of the Azerbaidzhan SSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 869-874, April, 1975. Original article submitted May 28, 1974.

© 1975 Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.



Fig. 1. Possible spatial structures of tetracyclic anhydrides and imides: A, B) trans; C, D) cis.

Within the framework of the simple additive scheme, for the methylated derivatives the insertion of alkyl radicals fails to affect the DM of the molecule, in view of which it is impossible to determine the spatial position of the CH₃ groups on the basis of the DM method. Compounds (II) and (VIII) were obtained from the anhydride of 3-methyl-4-cyclohexene-1,2-dicarboxylic acid, in which the methyl group has a cisposition relative to the C – CO bonds; (III) represents isomer (II) with a trans-orientation of the methyl group and anhydride ring. The spatial isomers (IV) and (V) should represent the addition products of the hexachlorocyclopentadiene molecule from the β -side of the syn- or anti-conformation forms of the dienophile, so that under the condition of endo-orientation, which is common for all of the known reactions of hexachlorocyclopentadiene, one of them has a trans-coupling of the cyclic fragments A and B, and the other has the cis-coupling C and D.

The DM were calculated for all of the possible spatial structures of the tetracyclic anhydrides and imides and a comparison was made with the experimentally determined values. In the calculations for the hexachlorocyclopentadiene adducts we used the value and direction of the total moment of the hexachlorocyclopentadiene system [7], taking into account the dipoles of the C - H bonds. For compounds (VII)-(IX) we took the DM of the carbonyl group as 2.83 D, which is equal to the DM of acetone, while the total DM of the four C - Cl bonds was calculated as the vector difference of the DM of the hexachlorocyclopentene system and the dichloromethylene group (2.20 D equals the DM of 2,2-dichloropropane). The DM of the anhydride ring is 4.37 D (the experimental value for the closest structural analog, the anhydride of 1,2-dimethylcyclohexene-4,5-dicarboxylic acid) [1], which is devoid of contributions by polar groups except C - H (the DM of the latter were included in the employed group DM); the DM of the N-phenylimide ring is 1.69 D, with a direction along the axis of symmetry of the five-membered ring [8]. In (X) and (XI) the DM of the dichlorovinylene bridge was assumed to be equal to 2.43 D, the experimentally determined DM of cis-2,3-dichloro-2-butene [9]. The dihedral angles between the planes, in which the coplanar bonds lie, was taken as 120°. The calculated and experimental DM values of (I)-(IX) are given in Table 1.

The configuration was determined previously for compounds (I) and (VII). The NMR spectra correspond to the existence of only one conformation of the molecule [5]. In calculating the DM of the molecules that contain a large number of strong dipoles it is impossible to obtain absolute agreement with the experimental results in the absence of accurate structural data. But within the limits of the accuracy of the method it is possible to choose in favor of the syn-conformation A in harmony with the conclusion made in [5]. The N-phenylimide derivative (VI) has such a structure. The insertion of a cis-CH₃ group in the 3 position of the 4-cyclohexene-1,2-dicarboxylic acid derivatives does not sterically affect the trans-addition of the diene molecule, so that compounds (II) and (VIII) should have the same configuration as the starting members of the series. The DM show little change when methyl groups are inserted, which indicates a retention not only of the trans-configuration, but also the syn-conformation of six-membered rings. It is obvious that (IX) has such a spatial structure. In these cases the CH₃ groups in the cis-positions to the C - CO bonds have an equatorial orientation, which can lead to additional stabilization of the syn-conformers.

An interesting case is (III), in which the CH₃ group and the anhydride rings are trans-oriented in such a manner that both sides of the double bond are sterically shielded, but to different degree, while the

.Compound	Calculated DM					
	trans-coupling		cis-coupling		Experimental	
	syn-A	anti B	syn C	anti D	DM	
(I)—(V)	5,03	2,54	6,48	2,54	$\begin{vmatrix} 4,32 & (I) \\ 4,44 & (II) \\ 2,62 & (III) \\ 4,26 & (IV) \end{vmatrix}$	
(VI) (VI1), (VIII) (IX)	3,02 5,56 3,52	1,37 2,02 1,44	4,08 6,55 - 4,32	1,37 2,02 1,44	$ \begin{vmatrix} 3,12 & (V) \\ 2,94 & (VI) \\ 5,00 & (VII) \\ 4,95 & (VIII) \\ 2,92 & (IX) \end{vmatrix} $	

TABLE 1. Dipole Moments, D, of Tetracyclic Anhydrides and Imides

molecule is being formed during the diene synthesis of hexachlorocyclopentadiene with the anhydride of trans-3-methyl-4-cyclohexene-cis-1,2-dicarboxylic acid. This compound has a small DM, which corresponds to the anti-conformation of the fragment of the cyclohexane ring, the five-membered ring with either a trans-B or a cis-D coupling of the rings. The trans-anti form D is sterically hindered [5]; the CH_3 group in it should occupy an axial position, i.e., it cannot assure a stabilization of the anti-conformation when compared with (I) and (II). It must be concluded that (III) is an isomer with a cis-arrangement of the hexa-chlorobicycloheptene system and the anhydride ring, and exists in the sterically unhindered conformation D with an equatorial orientation of the methyl.

When discussing the pairs of isomers (IV) and (V), which have methyl groups on the carbon atoms that are found in the anhydride ring, it is necessary to make assignment to the cis- and trans-series. The DM of (IV) is close to the DM of (I) and (II), which enables assigning it the trans-structure with a syn-conformation of the cyclohexane ring A. The equilibrium of the two conformations of the cis-isomer C = D, an alternate that satisfies experiment in this case, is hardly probable, since form C is sterically impossible. In such case, (V) has a cis-structure, and its polarity can be interpreted by anti-conformation D, the same as in the case of the cis-derivative (III). The fact that the experimental DM value is 0.6 D greater than the calculated, and 0.5 D greater than the DM of (III), cannot be considered to be an indication of the presence of syn-conformation C in view of its steric hindrance. It is possible that the addition of substituents to the carbon atom of the anhydride ring changes the geometry of the molecule somewhat.

However, it should be mentioned that the DM of (V) does not exclude structures of the trans-syn type, but with an exo-coupling of the bicycloheptene system and cyclohexane ring ($\mu_{calc} = 2.54$ D). To establish the structures we examined the steric relations of the isomeric 1,2,3,4,11,11-hexachloro-7-methyltricyclo[6.2.1.0^{5,10}]-2-undecene-7,8-dicarboxylic acids and their anhydrides. The reaction of hexachloro-cyclopentadiene with the anhydride of 1-methyl-4-cyclohexene-cis-1,2-dicarboxylic acid at temperatures below 160° gives adduct (IV), while at higher temperatures (V) is obtained in small amounts [10]. Based on the epimerization of the corresponding cis-diacids to various trans-isomers and an examination of the stereochemistry of the anhydride of trans-1,2,3,4,11,11-hexachloro-7-methyltricyclo[6.2.1.0^{5,10}]-2-un-decene-7,8-dicarboxylic acid (XII) we assigned the endo-trans structure to adduct (IV), and the exo-trans structure to (V). The endo-orientation of the diene, shown in [5], which corresponds to the known data on the structure of the hexachlorocyclopentadiene adducts, permits assuming the endo-structure for (XII) when reacted from the unshielded side of the double bond. The interconversions of the diacids of this series and their anhydrides can be depicted by the scheme shown in Fig. 2.

Since it is postulated that 1,2-diacids isomerize via the enol forms, the absence of interconversions between the cis-diacids and the isomeric trans-diacids with one carboxyl group on a tertiary carbon atom is fully understandable and should not serve as a reason for the differences in the configuration of the carbon skeleton. From Fig. 2 and the DM of (V) it follows that it should be assigned the endo-cis structure, with an anti-anti conformation of the central ring D.

When discussing the conformation of the cyclohexane rings in the pentacyclic dianhydrides (X) and (XI) it is necessary to consider the spatial structure of the starting products and the steric rules that lead to their formation by the diene synthesis reaction of maleic anhydride with the anhydrides of 1,2, 3,4-tetrachlorobicyclo[4.4.0]-2,4-decadiene-8,9-dicarboxylic acid and its 7-methyl derivative. Since the latter are formed by the decarbonylation of compounds (VII) and (VIII), the trans-orientation of the anhydride and cyclohexadiene rings is retained. Taking into account the endo-orientation of the addenda in the diene synthesis, the possibility of the maleic anhydride molecule approaching from either side of the diene system



Fig. 2. Steric relations in series of 1,2,3,4,11,11-hexachloro-7-methyltricyclo-2-undecene-7,8-dicarboxylic acids and their anhydrides.

(trans- from the unshielded side, and cis- from the side of the C-C bonds) and the possibility of the cyclohexane ring existing in two conformations, either syn- or anti- with respect to the anhydride ring for (X) and (XI), it follows that four possible structures must be considered (Fig. 3, R = H, CH_3).

The molecular DM calculated on the basis of the above given data have the following values: E 3.80, F 6.80, G 6.80, and H 3.80 D. The experimentally determined DM of (X) = 3.87, and (XI) = 4.19 D, correspond to those calculated for forms E and H, the choice between which is impossible. However, as can be seen from Fig. 3, the structures with an anti-conformation of the six-membered rings F and H are impossible due to the exceedingly close approach of the methine groups of the anhydride ring to the bridges of the bicyclooctene fragment. Consequently, compounds (X) and (XI) must be assigned structure E, which is formed as the result of the maleic anhydride molecule approaching from the unshielded side of the diene system, and which has the same syn-conformation of the cyclohexane ring as in the above described compounds. As a result, a cyclohexane ring that is condensed with a trans-arranged anhydride or imide ring and bicyclic system has the conformation of a bathtub, with an axial syn-orientation of the five-membered ring.

EXPERIMENTAL METHOD

The methods used to synthesize compounds (I) and (VII) are described in [5], those for (II)-(V) in [10], and those for (VIII), (X), and (XI) in [11]. Compound (VI), which has an N-phenylimide ring, was obtained by the acid hydrolysis of the N-phenylimide of 1,2,3,4-tetrachloro-11,11-dimethoxy-6-methyl-tricyclo[$6.2.1.0^{5,10}$]-2-undecene-7,8-dicarboxylic acid (XIII). The latter was synthesized by the imidation of the adduct of 5,5-dimethoxytetrachlorocyclopentadiene and the anhydride of cis,cis-3-methyl-4-cyclo-hexene-1,2-dicarboxylic acid (XIV) with aniline. Adduct (XIV) was obtained by the condensation of the indicated addenda at 140° for 16 h, using a 2:1 mole ratio of diene to dienophile. The obtained crystals were washed first with hot heptane, and then with MeOH. The yield of (XIII) was 90%, and mp 219°. Found: C 33.20%. C₁₄H₁₅Cl₄O₅. Calculated: Cl 33.02%.

Commound	4 = 1 4 20	$\Delta m_{\pi}^2 / \Delta w_{\pi}$	P. cm ³	u D
Compound	112/ 11W2		1 0, 0111	
(I)	5.099	0.084	387,333	4,32
dù	5,198	0.131	403,413	4,41
dìń	1.887	0.141	142,880	2,62
av	4,710	0.090	377,260	4,26
(v)	2 575	0.100	202,870	3,12
(Ŷń	2,103	0,186	179,229	2,94
(ÌÌÌÌ	7,694	0.157	520,965	5,00
(VIII)	7,210	0,097	507,998	4,95
(IX)	2 273	0,202	177,129	2,92
(\mathbf{x})	4.673	0.283	312,096	3,07
(ND)	5 239	0 277	365 017	4.19

TABLE 2. Dipole Moments of Studied Compounds



Fig. 3. Possible spatial structures of pentacyclic dianhydrides: E) trans-syn; F) trans-anti; G) cis-syn; H) cis-anti.

Anhydrides (I) and (XIV) were imidated by heating in DMF medium at 155° with an equimolar amount of aniline for 3 h. The mixture was poured into a beaker containing ice, and the obtained precipitate was filtered and recrystallized from ether. The yield of (IV) was 92%, and mp 221-222°. Found: Cl 42.47; N 2.68%. $C_{19}H_{13}Cl_6O_2N$. Calculated: Cl 42.60; N 2.80%. The yield of (XIII) was 94%, and mp 189-191°. Found: Cl 28.60; N 2.83%. $C_{21}H_{19}Cl_4O_4N$. Calculated: C 28.11; N 2.77%.

Ketoimide (IX) was obtained by the acid hydrolysis of N-phenylimide (XIII) with conc. H_2SO_4 at 20° for 3 h. The reaction mixture was diluted with ice water, filtered, and the isolated product was recrystallized from ether. The yield of (IX) was 93%, and mp 193-195° (decomp.). Found: Cl 30.00; N 2.97%. $C_{20}H_{15}Cl_4O_3N$. Calculated: Cl 30.90; N 3.06%.

The DM were determined by the second Debye method in benzene at 20°. The coefficients of the calculation equations [12] and the resulting values are given in Table 2.

CONCLUSIONS

1. When the cyclohexane ring is trans-condensed with a five-membered anhydride ring and a bicyclic system the C - C bonds of the bicyclic system occupy equatorial positions.

2. The stereochemistry of the diene synthesis of hexachlorocyclopentadiene with the anhydrides of cis- and trans-3-methyl-4-cyclohexene-1,2-dicarboxylic acids is determined by the configuration of the methyl group.

3. The addition of maleic anhydride to the diene system of the anhydride of 1,2,3,4-tetrachlorobicyclo[4.4.0]decadiene-8,9-dicarboxylic acid goes in the trans-position to the bonds of the cyclohexane ring.

LITERATURE CITED

- 1. A. N. Vereshchagin, A. P. Anastas'eva, and B. A. Arbuzov, Izv. Akad. Nauk SSSR, Ser. Khim., 995 (1970).
- 2. A. P. Anastas'eva, A. N. Vereshchagin, and B. A. Arbuzov, Izv. Akad. Nauk SSSR, Ser. Khim., 1709 (1970).
- 3. A. N. Vereshchagin, S. G. Vul'fson, L. S. Panfilova, A. A. Solov'ev, and B. A. Arbuzov, Izv. Akad. Nauk SSSR, Ser. Khim., 1575 (1972).
- 4. B. A. Arbuzov, L. A. Grozina, and A. N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 2370 (1969).
- 5. M. S. Salakhov, N. A. Alekperov, P. M. Poladov, Ya. S. Salakhova, M. M. Guseinov, and V. F. Kucherov, Zh. Organ. Khim., <u>9</u>, 842 (1973).
- 6. M. S. Salakhov, M. M. Guseinov, R. S. Salakhova, É. M. Treivus, and F. G. Akhundova, Azerb. Khim. Zh., No. 5, 76 (1971).
- 7. B. A. Arbuzov, A. N. Vereshchagin, and É. S. Batyeva, Izv. Akad. Nauk SSSR, Ser. Khim., 2080 (1966).

- 8. A. Arcona, H. Lumbroso, and R. Passerini, Bull. Soc. Chim. France, 754 (1959).
- 9. O. A. Osipov, V. I. Minkin, and A. D. Garnovskii, Handbook on Dipole Moments [in Russian], Vysshaya Shkola (1971).
- 10. M. S. Salakhov, T. O. Shamilov, A. I. Israfilov, M. M. Guseinov, and V. F. Kucherov, Problems in Stereochemistry [in Russian], Vol. 3, Kiev (1973), p. 126.
- 11. M. S. Salakhov, M. M. Guseinov, N. É. Musaeva, and N. A. Alekperov, Uch. Zap. Azerb. Gos. Univ., Ser. Khim., No. 2, 45 (1973).
- 12. É. Guggenheim and J. Prue, Physicochemical Calculations [Russian translation], IL (1958), p. 100.