Crystal Structure of 9-(5,5-Dimethyl-2,4,5,6-Tetrahydro-1*H*-Phenalen-2-yl)-5,5,9-Trimethyl-5,6,8,9-Tetrahydrocyclopenta[*a*]phenalen-10(4*H*)-one

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Abstract—The structure of 9-(5,5-dimethyl-2,4,5,6-tetrahydro-1*H*-phenalen-2-yl)-5,5,9-trimethyl-5,6,8,9-tetrahydrocyclopenta[*a*]phenalen-10(4*H*)-one was determined by X-ray crystallography. The intermolecular interaction energies were calculated by the atom-atomic approach for the crystal structure. The character of the crystal structure and the structural subclass were established.

INTRODUCTION

Organic compounds usually form crystals of lower syngonies—triclinic, monoclinic, and orthogonal [1, 2]. According to the long-established conclusions of Kitaygorodskiy [3], molecular crystals bound by weak van-der-Waals interaction show a tendency to form close molecular packing. The glide-reflection plane, screw axis 2_1, and center of inversion are the symmetry elements that best match the close packing [4]. The mentioned symmetry elements are second-order, which is why crystals of syngonies having no higher-order symmetry elements are mainly formed, i.e., crystals of lower symmetry classes. In more than 80% of cases, an organic molecule keeps its centrally symmetrical nature (if its higher symmetry is centrosymmetric), while other symmetry elements of the molecule are carried to the crystal quite rarely [5], and its conformation in the crystal becomes low-symmetrical.

Molecules are not "aware" of space groups, and their mutual arrangement in a crystal depends on the symmetry of the potential field around the molecule. This field is stationary only in the case of very rigid molecules; in the case of flexible molecules, it varies during the crystallization process. The resulting arrangement and conformation of molecules are assumed to correspond to the minimum of free energy of the crystal; more often, however, the minimum of the potential energy is mentioned in this context, allowing for the fact that the volume of the crystalline phase changes only slightly [6].

P.M. Zorkiy regarded a crystal as a hierarchical association of molecular agglomerates (islets, chains, layers) [7]. These agglomerates are distinguished in the crystal structure by analysis of the molecular interaction energy and its contribution to the total energy of the crystal. The structure is regarded as layered if the considered layers yield at least half the total crystal energy (the minimum efficiency of the layers is 50%); in a chain structure, at least one-third of the total energy should belong to the molecular chain (the minimum efficiency of the chains is 33%); dimers can be distinguished if their energy is at least one sixth of the total energy (the minimum efficiency of the dimers is 17%). It is assumed that with all other possibilities being the same, the crystal is formed with the minimum number of associations of agglomerates with different dimensionality. For example, if a given space group allows layer formation due to a strong molecular contact and consequent association of the layers in a three-dimensional structure due to a weaker interaction, then this scenario is preferable than the other in which the molecules first form chains, the chains unite into a layer, and only then the layers form a frame [6]. Certainly, here we consider not real crystallization stages but the observed result. If the molecular chains in the described example were energetically preferable over the layers, layers most likely would not form and the crystal would possess another space group.

The minimum number of unique intermolecular contacts necessary for crystal formation is called its critical coordination number (CCN) [8, 9]. This num-

Table 1. Crystallographic data for compound *A* and experimental parameters

Empirical formula	$C_{34}H_{36}O$
M_r	460.63
Syngony	Monoclinic
a, Å	15.2578(7)
b, Å	11.7041(6)
c, Å	29.8900(14)
α, deg	90
β, deg	94.7400(10)
γ, deg	90
V, Å^3	5319.5(4)
Space group	$C2/c$
Z	8
$F(000)$	1984
ρ_{calc}, g/cm^3	1.150
$\mu(MoK_\alpha)$, mm^{-1}	0.067
$2\theta_{max}$, deg	54
Experimental ranges hkl	$-19 \le h \le 19$, $-14 \le k \le 14$, $-38 \le l \le 38$
Number of measured reflexes	26916
Number of independent reflexes	5814
R_{int}	0.0435
Number of reflexes with $F > 4\sigma(F)$	4373
Number of parameters	321
wR_2	0.1362
$R_1(F > 4\sigma(F))$	0.0511
S	1.034
Residual electron density, $e \times$ Å^{-3} (d_{min}/d_{max})	0.391/−0.169

Table 2. Coordinates of non-hydrogen atoms ($\times 10^4$) and parameters of their isotropic shifts (Å$^2 \times 10^3$) for the compound *A*

Atom	x	y	z	U_{eq}
O(1)	3093(1)	4212(1)	2299(1)	34(1)
C(1)	2560(1)	5742(1)	2758(1)	25(1)
C(2)	1705(1)	6445(2)	2681(1)	29(1)
C(3)	1372(1)	6197(2)	2203(1)	25(1)
C(4)	685(1)	6761(2)	1950(1)	28(1)
C(5)	463(1)	6447(2)	1513(1)	26(1)
C(6)	−276(1)	7021(2)	1235(1)	31(1)
C(7)	−87(1)	7156(2)	743(1)	28(1)
C(8)	74(1)	5955(2)	563(1)	29(1)
C(9)	754(1)	5278(2)	848(1)	25(1)
C(10)	1212(1)	4406(2)	667(1)	29(1)
C(11)	1848(1)	3775(2)	926(1)	28(1)
C(12)	2051(1)	4041(1)	1369(1)	25(1)
C(13)	1609(1)	4944(1)	1570(1)	23(1)
C(14)	1822(1)	5316(1)	2021(1)	22(1)
C(15)	2544(1)	4958(1)	2343(1)	25(1)
C(17)	2594(1)	5016(1)	3191(1)	23(1)
C(18)	1811(1)	4240(1)	3194(1)	24(1)
C(19)	1478(1)	3881(1)	3571(1)	22(1)
C(20)	714(1)	3071(2)	3575(1)	25(1)
C(21)	893(1)	2115(1)	3922(1)	23(1)
C(22)	1058(1)	2680(1)	4385(1)	24(1)
C(23)	1721(1)	3636(1)	4404(1)	21(1)
C(24)	2144(1)	3972(2)	4813(1)	25(1)
C(25)	2734(1)	4874(2)	4836(1)	27(1)
C(26)	2918(1)	5446(2)	4449(1)	25(1)
C(27)	2510(1)	5125(1)	4035(1)	22(1)
C(28)	2667(1)	5766(2)	3611(1)	24(1)
C(29)	1906(1)	4219(1)	4012(1)	20(1)
C(30)	934(1)	5549(1)	1311(1)	23(1)
C(31)	3374(1)	6501(2)	2742(1)	34(1)
C(32)	1690(1)	1411(2)	3813(1)	30(1)
C(33)	88(1)	1345(2)	3925(1)	35(1)
C(34)	−887(1)	7682(2)	476(1)	40(1)
C(35)	714(1)	7924(2)	705(1)	31(1)

ber depends on the space group of the crystal and on the type of the system of symmetry-equivalent positions occupied by the molecules, i.e., the structural class of the crystal. The CCN shows the minimum number of agglomerates with different dimensionality in the structural subclass of the crystal [7]. The CCN of a crystal where molecules occupy the only possible system of equivalent positions is invariant for the space group. Here we try to answer the question whether the CCN coincides with the number of the strongest intermolecular contacts in a particular crystal structure. The object of the study was chosen, to an extent, accidentally: the studied compound was obtained at the Department of Organic Chemistry by senior researcher V.V. Izmer at one of the intermediate stages in the synthesis of new ligands for organometallic complexes tested as catalysts for olefin polymeriza-

tion. This material possesses the typical features of crystal structures of small organic molecules and hence was used in our calculation.

EXPERIMENTAL

An X-ray structural study of 9-(5,5-dimethyl-2,4,5,6-tetrahydro-1*H*-phenalen-2-yl)-5,5,9-trimethyl-5,6,8,9-tetrahydrocyclopenta[*a*]phenalen-10(4*H*)-one (**A**)

was carried out on a Bruker SMART APEX II auto-mated diffractometer with a coordinate detector [10] (MoK_α, graphite monochromator, ω-scanning) at a temperature of 120 K. Absorption was calculated semiempirically in the SADABS program [11]. The structure was obtained by direct methods and refined using the F^2 full least squares matrix in the anisotropic approximation for non-hydrogen atoms. All calculations were performed on a PC using the SHELXTL program [12]. Experimental parameters are listed in Table 1; atom coordinates are given in Table 2; the molecular structure of compound *A* is shown in Fig. 1.

Calculations

The energy of intermolecular interaction was calculated with Mercury software [13] in the atom-atomic approximation:

$$U_{\mathrm{mm}} = \Sigma\varphi_{ij},$$

where *i* and *j* are the indices of atoms belonging to different molecules. We used 6−exp atom-atom potentials with the Filippini−Gavezzotti parameters [14], which implicitly allow for electrostatic interactions:

$$\varphi_{ij} = -Cr_{ij} + A_{\exp}\left(-Br_{ij}\right).$$

The total energy U_Σ was found by summing the energy of pairwise interactions U_{MM} as the energy needed for an initial molecule to leave the crystal, calculated for 1 mol. The calculation involved the strongest 200 interactions, which reduces the series truncation error to a negligible level (less than 0.1%). To characterize molecular agglomerates, their efficiency was calculated as the ratio $U_{\mathrm{aggl}}/U_\Sigma$, where U_{aggl} is the net energy of interaction of a molecule in the agglomerate with its other molecules.

RESULTS AND DISCUSSION

A molecule of compound **A** is chiral and contains one asymmetrical atom C(1). It forms optically inactive crystals (racemate). The molecule contains two large polycyclic scaffolds which intersect at almost a right angle. The dihedral angle between the planes of aromatic fragments C(23)C(24)C(25)C(26)C(27)C(29) and C(13)C(14)C(3)C(4)C(5)C(30)C(9)C(10)C(11)C(12) (Fig. 1) is 81.6°. Meanwhile, the angle between the mean planes of large polyclical fragments (with three and four carbon cycles, respectively) is 81.4° (only slightly different). This geometry facilitates dimer formation, in which the mentioned molecular fragments interact closely as discussed below.

Crystals **A** belong to the $C2/c$ space group, monoclinic syngony, with $Z = 8(1)$ (all molecules occupy the single common system of equivalent positions). The molecule closest to the origin of the coordinate system (inside the unit cell) has the strongest contact with the molecule, which is symmetrically related to it
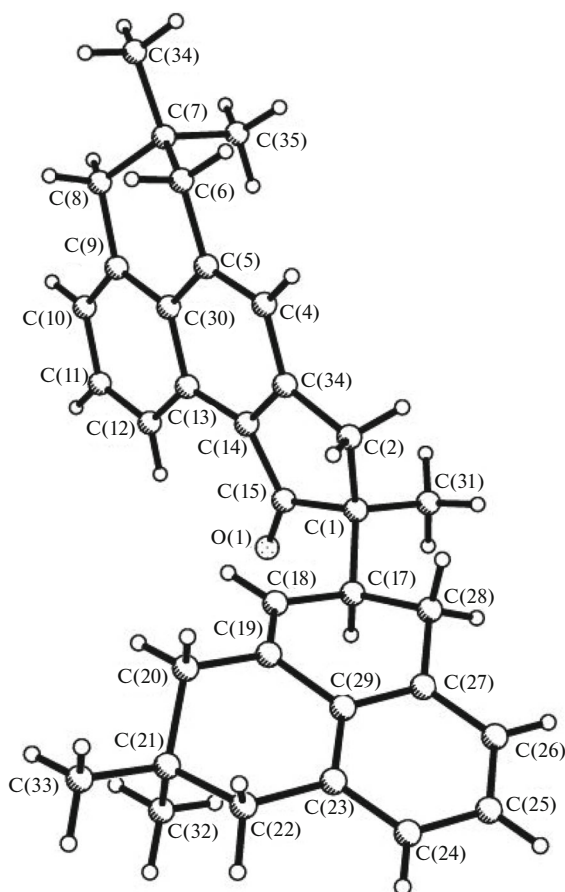

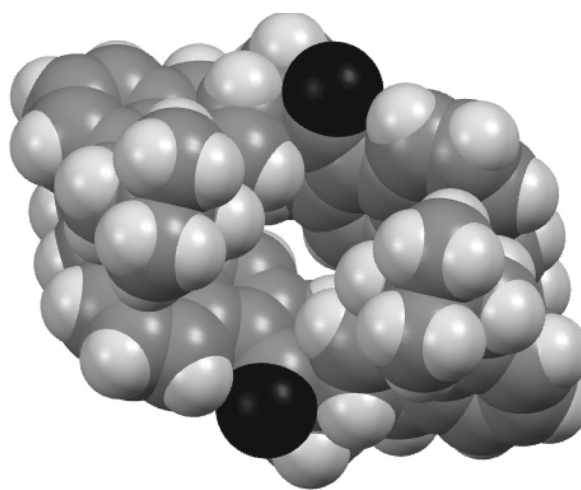**Fig. 1.** Molecular structure of compound *A*.

Fig. 2. Spherical model of dimer in crystal structure of *A* depicted in Bondi's van-der-Waals radii [15] (projection along axis *b*).

by the rotation axis 2 (0, *y*, 1/4), and forms a dimer ($U_{\mathrm{MM}} = -99.1$ kJ/mol), shown in Fig. 2.

The strongest pairwise atom−atom interactions exit in the dimmer are C(20)...C(30), C(9)...C(20),
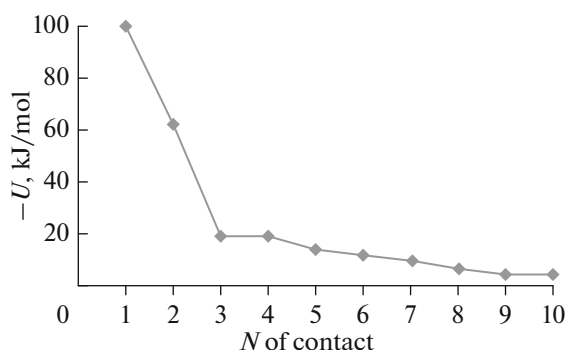
Fig. 3. Energies of strongest intermolecular contacts in crystal structure of A in descending order.

C(2)...C(4), C(8)...C(23), C(8)...C(29) with a distance of about 3.9 Å and $\varphi = -0.39$ kJ/mol. There are in total 57 relatively strong C...C interactions in the dimer with $|\varphi| \geq 0.30$ kJ/mol, and most of them are combined in pairs with respect to the rotation symmetry axis (28 pairs of equivalent interactions); the only single interaction is C(4)...C(4) 4.0 Å ($\varphi = -0.37$ kJ/mol), which intersects the rotation axis. The strongest of the C...H interactions is only number 105 in the rank of atom–atom potentials (C(6)...H2A, $\varphi = -0.21$ kJ/mol); the most intense C...O interaction is only number 561 (O(1)...C(20), $\varphi = -0.04$ kJ/mol). The latter is because oxygen atoms are oriented outside the dimer. The dimer energy is comprised of 5041 atom–atom potentials (allowing for equivalent pairs), among which only 11 are nonattractive (with $\varphi > 0$). There are 1906 weak potentials ($|\varphi| < 1$ J/mol).

The second strongest contact ($U_{MM} = -61.1$ kJ/mol) is between the initial molecule and two other molecules related to it by the screw axis 2_1 (1/4, y, 1/4); thus, a molecular chain is formed along this screw axis. If dimerization of the initial molecule in the (x, y, 1/4) plane is taken into account, a molecular layer with the symmetry $C_l 2$ can be distinguished. The third contact with $U_{MM} = -18.8$ kJ/mol corresponds to interaction between the mentioned layers: it binds the initial molecule and the molecule produced from it by a sliding reflection plane c (x, 1/2, z). The fourth contact is formed by the center of inversion i (1/4, 1/4, 1/2) and also connects the layers with each other ($U_{MM} = -18.4$ kJ/mol). The energies of the fifth and further contacts decrease monotonically (Fig. 3). The total energy of the crystal is $U_{\Sigma} = -259.8$ kJ/mol; the efficiency of the given layers is about 75%, and the efficiency of dimers combined into a layer is about 38%. Thus, the structure consists of dimers and at the same time it has a pronounced layered character (Fig. 4). Its structural subclass is

$$2 - C_l 2, \, Z = 4\,(1)\,C2/c, \, Z = 8\,(1).$$

The CCN for space group $C2/c$ with the only occupied system of positions of a common type is three [9]. It is noteworthy that the discontinuity of the curve $-U_{MM}(N)$ (Fig. 3) corresponds exactly to the third strong contact. It recalls the broken-stick rule in principal component analysis: a discontinuity of a curve showing the dependence of eigenvalues of linear combinations of components in some data array corresponds to the number of components describing most completely this array (the principal components) [16]. We can conclude that the number of strongest intermolecular contacts in a crystal structure tends to the minimum value, which is equal to the CCN.
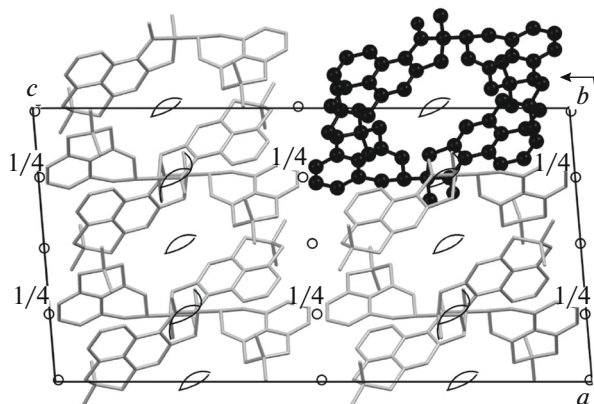
Fig. 4. Projection of crystal structure of A along axis b (ball-stick model). The dimer is shown in black color. Hydrogen atoms are not shown.

REFERENCES

1. Belsky, V.K., Zorkaya, O.N., and Zorky, P.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1995, vol. 51, p. 473.
2. Zorkii, P.M. and Oleinikov, P.N., *Zh. Fiz. Khim.*, 2000, vol. 74, p. 1944.
3. Kitaigorodskii, A.I., *Organicheskaya kristallokhimiya* (Organic Crystallochemistry), Moscow: Inst. Elementoorg. Soedin., Akad. Nauk SSSR, 1955.
4. Filippini, G. and Gavezzotti, A., *Acta Crystallogr., Sect. B: Struct. Sci.*, 1992, vol. 48, p. 230.
5. Pidcock, E., Motherwell, W.D.S., and Cole, J.C., *Acta Crystallogr., Sect. B: Struct. Sci.*, 2003, vol. 59, p. 634.
6. Zorky, P.M., *J. Mol. Struct.*, 1996, vol. 374, p. 9.
7. Zorkii, P.M. and Zorkaya, O.N., *J. Struct. Chem.*, 1998, vol. 39, no. 1, p. 103.
8. Banaru, A.M., *Moscow Univ. Chem. Bull. (Engl. Transl.)*, 2009, vol. 64, no. 2, p. 80.
9. Lord, E.E. and Banaru, A.M., *Moscow Univ. Chem. Bull. (Engl. Transl.)*, 2009, vol. 67, no. 2, p. 50.
10. APEX II Software Package, Bruker AXS, Madison, WI-53719, USA, 2005.
11. Sheldrick, G.M., SADABS, Bruker AXS, Madison, WI-53719, USA, 1997.
12. Sheldrick, G.M., SHELXTL: Structure Determination Software Suite, Bruker AXS, Madison, WI-53719, USA, 1998.
13. Macrae, C.F., Bruno, I.J., Chisholm, J.A., et al., *J. Appl. Crystallogr.*, 2008, vol. 41, p. 466.
14. Gavezzotti, A. and Filippini, G., *J. Phys. Chem.*, 1994, vol. 98, p. 4831.
15. Bondi, A., *J. Phys. Chem.*, 1964, vol. 68, p. 441.
16. Pomerantsev, A.L. and Rodionova, O.Ye., *J. Chemom.*, 2012, vol. 26, p. 299.

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