# Molecular structures and reactivities of 1,3-diphthalimidobenzene derivatives

*A. Yu. Kovalevsky,[a]* O. V. Shishkin,[b] and I. I. Ponomarev[a]*

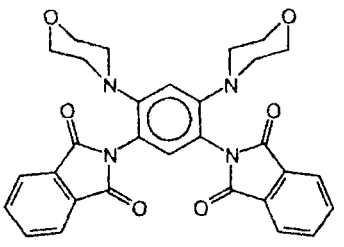
*[a]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: +7 (095) 135 5085. E-mail: xray@xray.ineos.ac.ru*

*[b]Institute for Single Crystals, Ukrainian National Academy of Sciences, 60 prosp. Lenina, 310001 Kharkov, Ukraine. Fax: +38 (057 2) 32 0273. E-mail: shishkin@isc.kharkov.com*

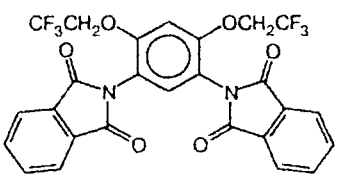
X-ray diffraction analysis of 4,6-di(morpholin-4-yl) and 4,6-di(2,2,2-trifluoroethoxy) derivatives of 1,3-diphthalimidobenzene, which are potent reagents in the synthesis of heterocyclic polymers, was carried out. The conjugation between the π-systems of the benzene ring and of the phthalimide and morpholine substituents is distorted due to the rotation of the substituents about the C(Ar)—N bonds. The AM1 calculations demonstrated that the hydrogen atoms of the methylene groups are "acidic," which is favorable for condensation reactions. Steric hindrances to intramolecular condensation were estimated.

**Key words:** molecular structure, 1,3-diphthalimidobenzene, AM1 method, charge distribution.

Aromatic polyimides belong to the class of valuable thermostable polymers, which exhibit a number of specific properties, including electrophysical properties, optical properties, *etc.*[1] The presence of different side substituents in these polymers allows one to vary their physical and chemical properties within wide limits.[2] A knowledge of the conformational characteristics and the electronic structures of monomer units, which form macromolecules, is of primary importance for explaining particular properties of polymers. With the aim of studying these characteristics of amino and amido derivatives of benzene, we studied the molecular and electronic structures of model compounds **1** and **2**.



**1**




**2**

## Experimental

Compounds **1** and **2** were prepared according to a known procedure.[3]

**X-ray diffraction analysis.** Crystals of compound **1**, $C_{30}H_{26}N_4O_6$, are triclinic. At −120 °C, $a$ = 11.094(3) Å, $b$ = 11.096(3) Å, $c$ = 11.801(2) Å, α = 87.01(2)°, β = 70.45(2)°, γ = 79.27(2)°, $V$ = 1344.9(6) Å$^3$, $d_{calc}$ = 1.330 g cm$^{-3}$, μ = 0.094 mm$^{-1}$, space group $P\bar{1}$, $Z$ = 2. The unit cell parameters and intensities of 6031 reflections (4909 independent reflections, $R_{int}$ = 0.033) were measured on an automated four-circle Siemens P3/PC diffractometer (graphite monochromator, Mo-Kα radiation, θ/2θ scanning technique, $2\theta_{max}$ = 54°).

The structure was solved by the direct method using the SHELXTL PLUS 5.02 program package.[4] The positions of the hydrogen atoms were located from the difference electron density synthesis and refined using the riding model with variable $U_{iso}$. The structure was refined based on $F^2$ by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms using 3272 reflections. The final values of the $R$ factors were as follows: $R_1$ = 0.068 (based on 2606 reflections with $F > 4\sigma(F)$), $wR_2$ = 0.134, $S$ = 1.25. The atomic coordinates, bond lengths, and bond angles are given in Tables 1—3, respectively.

Crystals of compound **2**, $C_{28}H_{14}N_2O_6F_6 \cdot 0.3C_6H_{14}O_2$, are triclinic. At −86 °C, $a$ = 13.907(5) Å, $b$ = 16.247(7) Å, $c$ = 16.503(8) Å, α = 98.62(3)°, β = 94.56(3)°, γ = 93.29(3)°, $V$ = 4110(3) Å$^3$, $d_{calc}$ = 1.464 g cm$^{-3}$, μ = 0.131 mm$^{-1}$, space group $P\bar{1}$, $Z$ = 6. The unit cell parameters and intensities of 12057 reflections (11351 independent reflections, $R_{int}$ = 0.054) were measured on an automated four-circle Syntex $P2_1$ diffractometer (graphite monochromator, Mo-Kα radiation, θ/2θ scanning technique, $2\theta_{max}$ = 52°). We carried out the profile analysis of the X-ray diffraction data according to a known procedure,[5] which made it possible to improve substantially the quality of the data set.

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**Table 1.** Coordinates of nonhydrogen atoms ($\times 10^4$) and their equivalent isotropic thermal parameters ($\times 10^3/Å^2$) in the structure of **1**

| Atom | x | y | z | $U_{eq}$ | Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|
| N(1) | 1710(3) | 1693(2) | 4510(2) | 46(1) | C(11) | −811(4) | 663(4) | 2444(4) | 77(1) |
| N(2) | 2418(3) | 3714(2) | 7726(2) | 45(1) | C(12) | −676(4) | 1666(4) | 3016(4) | 65(1) |
| N(3) | 5101(3) | 3400(2) | 6420(2) | 45(1) | C(13) | 258(3) | 1481(3) | 3560(3) | 49(1) |
| N(4) | 4271(3) | 1656(2) | 3053(2) | 48(1) | C(14) | 702(3) | 2358(3) | 4165(3) | 54(1) |
| O(1) | 2685(3) | −350(2) | 4468(2) | 67(1) | C(15) | 2448(3) | 4938(3) | 7938(3) | 51(1) |
| O(2) | 319(3) | 3453(2) | 4319(3) | 78(1) | C(16) | 1945(3) | 5102(3) | 9268(3) | 48(1) |
| O(3) | 1742(3) | 2055(2) | 8868(2) | 65(1) | C(17) | 1796(4) | 6117(4) | 9954(4) | 66(1) |
| O(4) | 2777(3) | 5689(2) | 7188(2) | 72(1) | C(18) | 1288(4) | 6009(5) | 11184(4) | 75(1) |
| O(5) | 7202(3) | 3605(3) | 7209(3) | 83(1) | C(19) | 949(4) | 4932(5) | 11702(4) | 76(1) |
| O(6) | 5523(3) | 1335(3) | 538(2) | 80(1) | C(20) | 1094(4) | 3902(4) | 11012(3) | 63(1) |
| C(1) | 2556(3) | 2193(3) | 4956(3) | 45(1) | C(21) | 1608(3) | 4020(3) | 9776(3) | 46(1) |
| C(2) | 2096(4) | 2720(3) | 6094(3) | 50(1) | C(22) | 1897(3) | 3103(3) | 8801(3) | 47(1) |
| O(3) | 2930(3) | 3136(3) | 6559(3) | 44(1) | C(23) | 5316(4) | 2700(3) | 7443(3) | 55(1) |
| C(4) | 4261(3) | 3000(3) | 5920(3) | 43(1) | C(24) | 5996(5) | 3380(4) | 8034(4) | 80(1) |
| C(5) | 4690(3) | 2506(3) | 4751(3) | 48(1) | C(25) | 6345(4) | 3630(3) | 5586(3) | 54(1) |
| C(6) | 3856(3) | 2131(3) | 4257(3) | 45(1) | C(26) | 6988(4) | 4293(4) | 6219(4) | 68(1) |
| C(7) | 1916(4) | 438(3) | 4210(3) | 50(1) | C(27) | 5627(4) | 1066(4) | 2557(3) | 72(1) |
| C(8) | 1011(3) | 339(3) | 3561(3) | 48(1) | C(28) | 5834(4) | 469(4) | 1359(3) | 76(1) |
| C(9) | 863(4) | −662(3) | 3005(3) | 64(1) | C(29) | 3940(4) | 2541(3) | 2200(3) | 65(1) |
| C(10) | −56(4) | −474(4) | 2428(4) | 75(1) | C(30) | 4196(5) | 1896(4) | 1028(3) | 88(2) |

**Table 2.** Bond lengths in the structure of **1**

| Bond | d/Å | Bond | d/Å | Bond | d/Å | Bond | d/Å | Bond | d/Å |
|---|---|---|---|---|---|---|---|---|---|
| N(1)—C(14) | 1.389(4) | N(4)—C(6) | 1.435(4) | O(6)—C(28) | 1.409(4) | C(8)—C(9) | 1.381(5) | C(16)—C(17) | 1.374(5) |
| N(1)—C(7) | 1.413(4) | N(4)—C(27) | 1.455(5) | O(6)—C(30) | 1.420(5) | C(8)—C(13) | 1.383(5) | C(17)—C(18) | 1.378(6) |
| N(1)—C(1) | 1.422(4) | N(4)—C(29) | 1.457(4) | C(1)—C(2) | 1.385(4) | C(9)—C(10) | 1.385(5) | C(18)—C(19) | 1.372(6) |
| N(2)—C(15) | 1.401(4) | O(1)—C(7) | 1.206(4) | C(1)—C(6) | 1.392(5) | C(10)—C(11) | 1.376(6) | C(19)—C(20) | 1.391(6) |
| N(2)—C(22) | 1.403(4) | O(2)—C(14) | 1.212(4) | C(2)—C(3) | 1.376(5) | C(11)—C(12) | 1.388(6) | C(20)—C(21) | 1.386(5) |
| N(2)—C(3) | 1.437(4) | O(3)—C(22) | 1.201(4) | C(3)—C(4) | 1.398(5) | C(12)—C(13) | 1.371(5) | C(21)—C(22) | 1.489(4) |
| N(3)—C(4) | 1.402(4) | O(4)—C(15) | 1.196(4) | C(4)—C(5) | 1.404(4) | C(13)—C(14) | 1.478(5) | C(23)—C(24) | 1.498(5) |
| N(3)—C(25) | 1.461(4) | O(5)—C(24) | 1.423(5) | C(5)—C(6) | 1.377(5) | C(15)—C(16) | 1.488(5) | C(25)—C(26) | 1.489(5) |
| N(3)—C(23) | 1.464(4) | O(5)—C(26) | 1.424(5) | C(7)—C(8) | 1.473(5) | C(16)—C(21) | 1.372(5) | C(27)—C(28) | 1.521(5) |
| | | | | | | | | C(29)—C(30) | 1.507(5) |

**Table 3.** Bond angles in the structure of **1**

| Angle | ω/deg | Angle | ω/deg | Angle | ω/deg | Angle | ω/deg |
|---|---|---|---|---|---|---|---|
| C(14)—N(1)—C(7) | 110.9(3) | C(3)—C(2)—C(1) | 120.3(3) | C(8)—C(9)—C(10) | 117.4(4) | C(19)—C(18)—C(17) | 121.4(4) |
| C(14)—N(1)—C(1) | 125.9(3) | C(2)—C(3)—C(4) | 121.3(3) | C(11)—C(10)—C(9) | 120.7(4) | C(18)—C(19)—C(20) | 121.7(4) |
| C(7)—N(1)—C(1) | 122.7(3) | C(2)—C(3)—N(2) | 119.1(3) | C(10)—C(11)—C(12) | 121.9(4) | C(21)—C(20)—C(19) | 116.5(4) |
| C(15)—N(2)—C(22) | 111.7(3) | C(4)—C(3)—N(2) | 119.6(3) | C(13)—C(12)—C(11) | 117.1(4) | C(16)—C(21)—C(20) | 121.3(3) |
| C(15)—N(2)—C(3) | 124.2(3) | C(3)—C(4)—N(3) | 120.5(3) | C(12)—C(13)—C(8) | 121.4(3) | C(16)—C(21)—C(22) | 108.9(3) |
| C(22)—N(2)—C(3) | 124.1(3) | C(3)—C(4)—C(5) | 117.1(3) | C(12)—C(13)—C(14) | 130.5(3) | C(20)—C(21)—C(22) | 129.8(3) |
| C(4)—N(3)—C(25) | 116.9(3) | N(3)—C(4)—C(5) | 122.4(3) | C(8)—C(13)—C(14) | 108.1(3) | O(3)—C(22)—N(2) | 125.1(3) |
| C(4)—N(3)—C(23) | 116.1(3) | C(6)—C(5)—C(4) | 122.1(3) | O(2)—C(14)—N(1) | 124.6(3) | O(3)—C(22)—C(21) | 129.6(3) |
| C(25)—N(3)—C(23) | 109.4(3) | C(5)—C(6)—C(1) | 119.0(3) | O(2)—C(14)—C(13) | 128.8(3) | N(2)—C(22)—C(21) | 105.4(3) |
| C(6)—N(4)—C(27) | 116.3(3) | C(5)—C(6)—N(4) | 122.9(3) | N(1)—C(14)—C(13) | 106.6(3) | N(3)—C(23)—C(24) | 109.7(3) |
| C(6)—N(4)—C(29) | 113.6(3) | C(1)—C(6)—N(4) | 118.0(3) | O(4)—C(15)—N(2) | 126.1(3) | O(5)—C(24)—C(23) | 111.4(3) |
| C(27)—N(4)—C(29) | 109.8(3) | O(1)—C(7)—N(1) | 124.4(3) | O(4)—C(15)—C(16) | 128.1(3) | N(3)—C(25)—C(26) | 109.9(3) |
| C(24)—O(5)—C(26) | 109.9(3) | O(1)—C(7)—C(8) | 129.8(3) | N(2)—C(15)—C(16) | 105.8(3) | O(5)—C(26)—C(25) | 111.1(3) |
| C(28)—O(6)—C(30) | 109.0(3) | N(1)—C(7)—C(8) | 105.9(3) | C(21)—C(16)—C(17) | 121.9(3) | N(4)—C(27)—C(28) | 108.6(3) |
| C(2)—C(1)—C(6) | 119.9(3) | C(9)—C(8)—C(13) | 121.4(3) | C(21)—C(16)—C(15) | 108.3(3) | O(6)—C(28)—C(27) | 111.6(3) |
| C(2)—C(1)—N(1) | 120.2(3) | C(9)—C(8)—C(7) | 130.1(3) | C(17)—C(16)—C(15) | 129.8(4) | N(4)—C(29)—C(30) | 109.3(3) |
| C(6)—C(1)—N(1) | 119.9(3) | C(13)—C(8)—C(7) | 108.4(3) | C(16)—C(17)—C(18) | 117.2(4) | O(6)—C(30)—C(29) | 110.9(4) |

The structure was solved by the direct method using the SHELXTL PLUS 5.02 program package.[4] The positions of the hydrogen atoms were calculated geometrically and refined using the riding model with variable $U_{iso}$. The structure was

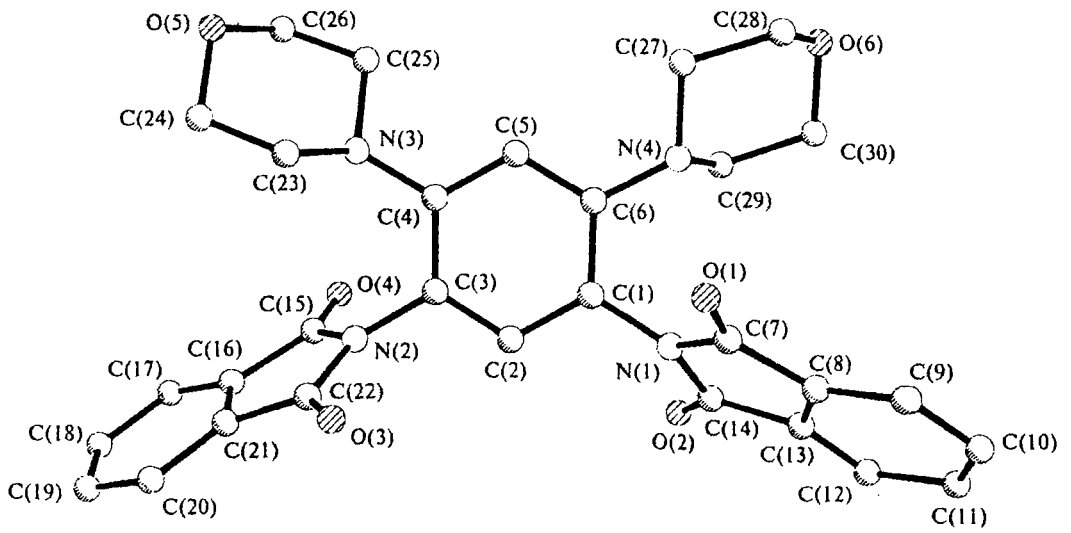



**Fig. 1.** Structure of compound **1**.

refined based on $F^2$ by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms using 11258 reflections. The final values of the $R$ factors were as follows: $R_1 = 0.095$ (based on 5901 reflections with $F > 4\sigma(F)$), $wR_2 = 0.261$, $S = 1.07$. The nonhydrogen atoms of the molecule of solvation were refined with fixed values of the bond lengths, which were best approximated to their mean values[6] (C—C, 1.54(1) Å; C —O 1.36(1) Å). The atomic coordinates, bond lengths, and bond angles (averaged over three independent molecules) are given in Tables 4—6, respectively.

**Quantum-chemical calculations.** The spatial structures and the charge distributions in molecules **1**—**9** were calculated by the semiempirical quantum-chemical AM1 method[7] with full geometry optimization. The results of calculations are given in Scheme 1.

## Results and Discussion

The saturated heterocycles in molecule **1** (Fig. 1) adopt an almost ideal chair conformation (the endocyclic torsion angles are in the range of 56—60°). The angles between the mean planes of the benzene ring and of the central fragments of the morpholine groups, C(23)...C(26) and C(27)...C(30), are 44.4° and 52.6°, respectively. The phthalimide substituents are planar and are rotated with respect to the plane of the aromatic ring (the C(4)—C(3)—N(2)—C(15) and C(6)—C(1)—N(1)—C(7) torsion angles are 63.4(4)° and 61.0(4)°, respectively). This arrangement of the saturated rings and the phthalimide fragments is, apparently, dictated by steric repulsions between the *ortho*-substituents, which results in the shortened intramolecular contacts: H(23A)...C(3), 2.79 Å (the sum of the van der Waals radii[8] (Svdw) is 2.87 Å); H(25A)...C(5), 2.73 Å; H(25B)...C(5), 2.82 Å; H(27B)...C(5), 2.78 Å; H(29B)...C(1), 2.84 Å; H(25A)...H(5A), 2.27 Å (Svdw 2.32 Å); H(27B)...H(5A), 2.21 Å; N(2)...H(23A) 2.51 Å (Svdw 2.66 Å); and C(14)...H(29B), 2.80 Å (Svdw 2.87 Å).

The difference in the angles of rotation of the morpholine substituents is worthy of note. The AM1 calculations of the equilibrium geometry of the isolated molecule demonstrated that in the gaseous phase, the angles of rotation of both saturated heterocycles and of the phthalimide substituents are equal (90±6°), and the molecule as a whole has an approximate twofold axis, which passes through the C(2) and C(5) atoms. Therefore, the distortion of the molecular symmetry in the crystal is, apparently, accounted for by the effects of the crystal packing.

In the crystal, molecules **1** are linked in dimers *via* the weak intermolecular shortened contacts O(4)...H(25'A) (1 − $x$, 1 − $y$, 1 − $z$) (2.38 Å; the sum of the van der Waals radii is 2.45 Å)[8] with the participation of the hydrogen atoms of one of the morpholine substituents.

There are three independent molecules (**A**, **B**, and **C**) in the asymmetric unit of the crystal of compound **2**. Molecules **A** and **B** adopt similar conformations, while the conformation of **C** differs substantially from those of **A** and **B**.

In molecules **A** and **B**, the phthalimide substituents are planar (Fig. 2), except for this group at the C(6') atom in molecule **B**, in which the five-membered ring adopts a flattened envelope conformation (the N(2') atom deviates from the plane through the remaining atoms of the ring by −0.07 Å). The angles of rotation of the phthalimide substituents with respect to the benzene rings are similar to those observed in **1** (the C(1)—C(2)—N(1)—C(7) and C(1)—C(6)—N(2)—C(22) torsion angles are 48.7(8)° and 55.6(8)° (**A**), and 60.2(7)° and 54.9(8)° (**B**), respectively).

The methylene groups of the trifluoroethyl substituents are in an *sp* conformation with respect to the plane of the benzene ring (the C(4)—C(3)—O(6)—C(25) and C(4)—C(5)—O(5)—C(23) torsion angles are −2.8(8)°

**Table 4.** Coordinates of nonhydrogen atoms ($\times 10^4$) and their equivalent isotropic thermal parameters ($\times 10^3/Å^2$) in the structure of **2**

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| N(1) | 7432(4) | −11212(3) | 2095(2) | 36(1) |
| N(2) | 5317(3) | −12389(2) | −74(2) | 36(1) |
| O(1) | 8598(3) | −11577(3) | 1293(2) | 63(1) |
| O(2) | 6626(4) | −11045(2) | 3146(2) | 47(1) |
| O(3) | 5145(3) | −13515(2) | 544(2) | 58(1) |
| O(4) | 5498(3) | −11591(2) | −993(2) | 43(1) |
| O(5) | 4156(3) | −11097(2) | 188(2) | 41(1) |
| O(6) | 6499(3) | −9783(2) | 2171(2) | 49(1) |
| C(1) | 6366(4) | −11785(3) | 1003(3) | 36(2) |
| C(2) | 6643(4) | −11144(3) | 1584(3) | 35(2) |
| C(3) | 6120(4) | −10428(3) | 1649(3) | 35(2) |
| C(4) | 5285(4) | −10383(3) | 1193(3) | 33(2) |
| C(5) | 4974(4) | −11063(3) | 644(3) | 34(2) |
| C(6) | 5552(4) | −11742(3) | 530(3) | 32(2) |
| C(7) | 8340(6) | −11453(3) | 1914(4) | 47(2) |
| C(8) | 8896(6) | −11534(4) | 2611(4) | 50(2) |
| C(9) | 9812(7) | −11768(5) | 2747(5) | 76(2) |
| C(10) | 10144(7) | −11836(5) | 3466(6) | 92(3) |
| C(11) | 9542(8) | −11680(5) | 4017(5) | 83(3) |
| C(12) | 8608(6) | −11453(4) | 3886(4) | 62(2) |
| C(13) | 8295(5) | −11388(3) | 3169(3) | 45(2) |
| C(14) | 7358(6) | −11196(3) | 2847(3) | 38(2) |
| C(15) | 5182(5) | −13234(3) | −25(3) | 45(2) |
| C(16) | 5086(5) | −13686(3) | −790(3) | 42(2) |
| C(17) | 4949(5) | −14519(3) | −1067(3) | 56(2) |
| C(18) | 4913(5) | −14746(4) | −1823(3) | 61(2) |
| C(19) | 5001(5) | −14165(4) | −2280(3) | 53(2) |
| C(20) | 5152(5) | −13323(4) | −2007(3) | 44(2) |
| C(21) | 5197(4) | −13095(3) | −1255(3) | 36(2) |
| C(22) | 5354(4) | −12259(3) | −806(3) | 32(1) |
| C(23) | 3501(5) | −10477(3) | 342(3) | 41(2) |
| C(24) | 2579(6) | −10764(4) | −110(3) | 55(2) |
| C(25) | 6048(4) | −9020(3) | 2231(3) | 37(2) |
| C(26) | 6748(5) | −8387(4) | 2685(3) | 45(2) |
| F(1) | 2181(3) | −11459(3) | 61(3) | 100(2) |
| F(2) | 1917(3) | −10215(3) | −10(2) | 96(2) |
| F(3) | 2679(3) | −10925(3) | −818(3) | 80(1) |
| F(4) | 6348(3) | −7679(2) | 2832(2) | 78(1) |
| F(5) | 7523(3) | −8236(2) | 2329(2) | 72(1) |
| F(6) | 7079(3) | −8613(2) | 3304(2) | 77(1) |
| N(1′) | 7424(4) | −10869(3) | −3136(3) | 37(1) |
| N(2′) | 4759(3) | −12467(2) | −4704(2) | 34(1) |
| O(1′) | 8273(3) | −11343(2) | −4128(2) | 50(1) |
| O(2′) | 7071(4) | −10391(3) | −1952(2) | 55(1) |
| O(3′) | 4795(3) | −13324(2) | −3799(2) | 48(1) |
| O(4′) | 4749(3) | −12051(2) | −5842(2) | 49(1) |
| O(5′) | 3782(3) | −11090(2) | −4643(2) | 49(1) |
| O(6′) | 6448(3) | −9488(2) | −3104(2) | 53(1) |
| C(1′) | 6075(5) | −11666(3) | −3895(3) | 36(2) |
| C(2′) | 6477(5) | −10925(3) | −3501(3) | 34(2) |
| C(3′) | 5975(5) | −10201(3) | −3482(3) | 42(2) |
| C(4′) | 5074(5) | −10241(3) | −3864(3) | 43(2) |
| C(5′) | 4672(5) | −10988(4) | −4257(3) | 41(2) |
| C(6′) | 5181(5) | −11710(3) | −4283(3) | 36(2) |
| C(7′) | 8266(5) | −11039(3) | −3494(3) | 37(2) |
| C(8′) | 9088(7) | −10798(3) | −2931(3) | 40(2) |
| C(9′) | 10075(7) | −10838(4) | −2986(4) | 58(2) |
| C(10′) | 10678(6) | −10550(5) | −2355(6) | 76(2) |
| C(11′) | 10301(9) | −10247(4) | −1693(5) | 77(3) |
| C(12′) | 9315(7) | −10203(4) | −1642(4) | 56(2) |
| C(13′) | 8734(6) | −10489(3) | −2280(3) | 36(2) |
| C(14′) | 7691(7) | −10554(3) | −2387(3) | 45(2) |
| C(15′) | 4609(4) | −13227(3) | −4421(3) | 36(2) |
| C(16′) | 4230(4) | −13848(3) | −5071(3) | 33(2) |
| C(17′) | 3947(4) | −14681(3) | −5116(3) | 43(2) |
| C(18′) | 3648(5) | −15125(4) | −5812(3) | 49(2) |
| C(19′) | 3615(4) | −14736(4) | −6424(3) | 48(2) |
| C(20′) | 3891(5) | −13902(4) | −6381(3) | 46(2) |
| C(21′) | 4204(4) | −13467(3) | −5687(3) | 36(2) |
| C(22′) | 4585(4) | −12570(3) | −5459(3) | 38(2) |
| C(23′) | 3243(5) | −10390(3) | −4687(3) | 42(2) |
| C(24′) | 2298(5) | −10709(4) | −5073(4) | 50(2) |
| C(25′) | 5892(5) | −8834(3) | −2841(3) | 45(2) |
| C(26′) | 6537(6) | −8171(4) | −2383(4) | 58(2) |
| F(1′) | 2376(4) | −11140(4) | −5720(3) | 145(3) |
| F(2′) | 1802(3) | −11202(3) | −4755(3) | 101(2) |
| F(3′) | 1765(4) | −10110(3) | −5193(3) | 126(2) |
| F(4′) | 7229(4) | −7889(3) | −2740(3) | 109(2) |
| F(5′) | 6955(4) | −8423(3) | −1795(3) | 127(2) |
| F(6′) | 6072(3) | −7525(2) | −2135(2) | 92(2) |
| N(1″) | 8033(4) | −3706(2) | 4427(2) | 31(1) |
| N(2″) | 8785(4) | −3054(3) | 7090(3) | 35(1) |
| O(1″) | 6526(3) | −3298(2) | 4708(2) | 45(1) |
| O(2″) | 9362(4) | −4026(3) | 3805(2) | 71(2) |
| O(3″) | 7161(4) | −2918(3) | 7201(3) | 63(2) |
| O(4″) | 10447(4) | −3068(3) | 7351(3) | 70(2) |
| O(5″) | 8989(3) | −4659(2) | 7136(2) | 54(1) |
| O(6″) | 8349(3) | −5324(2) | 4500(2) | 40(1) |
| C(1″) | 8471(4) | −3366(3) | 5755(3) | 33(2) |
| C(2″) | 8356(4) | −3949(3) | 5111(3) | 32(1) |
| C(3″) | 8512(4) | −4787(3) | 5143(3) | 35(2) |
| C(4″) | 8764(4) | −5030(3) | 5805(3) | 33(2) |
| C(5″) | 8827(4) | −4462(3) | 6439(3) | 35(2) |
| C(6″) | 8706(4) | −3633(3) | 6419(3) | 36(2) |
| C(7″) | 7117(5) | −3423(3) | 4267(3) | 31(2) |
| C(8″) | 7059(5) | −3352(3) | 3483(3) | 31(2) |
| C(9″) | 6300(5) | −3120(3) | 3038(3) | 38(2) |
| C(10″) | 6423(5) | −3181(4) | 2295(3) | 49(2) |
| C(11″) | 7255(6) | −3446(4) | 2015(3) | 52(2) |
| C(12″) | 8009(5) | −3664(4) | 2457(3) | 55(2) |
| C(13″) | 7907(5) | −3617(3) | 3203(3) | 40(2) |
| C(14″) | 8548(6) | −3805(4) | 3805(3) | 46(2) |
| C(15″) | 7986(7) | −2806(4) | 7465(4) | 38(2) |
| C(16″) | 8384(6) | −2417(3) | 8203(3) | 37(2) |
| C(17″) | 7925(6) | −2060(4) | 8795(4) | 59(2) |
| C(18″) | 8508(8) | −1755(4) | 9443(4) | 70(2) |
| C(19″) | 9489(8) | −1800(4) | 9490(4) | 70(2) |
| C(20″) | 9952(6) | −2150(4) | 8892(4) | 63(2) |
| C(21″) | 9352(6) | −2453(3) | 8250(3) | 42(2) |
| C(22″) | 9661(7) | −2891(4) | 7544(3) | 45(2) |
| C(23″) | 8983(6) | −5489(5) | 7227(4) | 74(2) |
| C(24″) | 8825(13) | −5558(9) | 7974(6) | 134(5) |
| C(25″) | 8965(4) | −6000(3) | 4370(3) | 36(2) |
| C(26″) | 8441(6) | −6815(4) | 4446(4) | 57(2) |
| F(1″) | 8073(7) | −5264(7) | 8197(4) | 217(5) |
| F(2″) | 9604(7) | −5154(5) | 8411(3) | 177(3) |
| F(3″) | 8883(6) | −6360(5) | 8084(4) | 190(3) |
| F(4″) | 7614(4) | −6948(3) | 4035(3) | 96(2) |
| F(5″) | 8218(3) | −6865(2) | 5130(2) | 87(1) |
| F(6″) | 8987(3) | −7433(2) | 4240(2) | 85(1) |
| O(1S) | 8210(9) | −4888(8) | 14(6) | 226(4) |
| O(2S) | 7613(6) | −5708(5) | 1160(5) | 168(3) |
| C(1S) | 7353(12) | −5387(10) | −44(9) | 240(8) |
| C(2S) | 7494(11) | −6085(8) | 436(6) | 175(5) |
| C(3S) | 8244(9) | −4039(8) | 78(8) | 180(5) |
| C(4S) | 9275(11) | −3658(10) | 234(9) | 63(5) |
| C(4S′) | 7402(8) | −3548(6) | 73(5) | 53(3) |
| C(5S) | 7607(8) | −6328(6) | 1596(5) | 130(4) |
| C(6S) | 7730(9) | −5860(7) | 2377(5) | 143(4) |

and −10.3(8)°, respectively, in molecule **A** and 25.7(8)° and 3.7(8)°, respectively, in molecule **B**) in spite of the shortened intramolecular contacts H(4A)...H(23B) (2.26 Å; the sum of the van der Waals radii[8] is 2.32 Å), H(4A)...H(25A) (2.13 Å (molecule **A**)), H(4'A)...H(23D) (2.23 Å), and H(4'A)...H(25D) (2.22 Å (molecule **B**)). The presence of these contacts in molecule **A** causes the deviations of the O(5) and O(6) atoms from the plane of the benzene ring by 0.11 and −0.15 Å, respectively.

The trifluoromethyl groups are in an antiperiplanar (*ap*) conformation with respect to the O—C(Ar) bonds (the C(3)—O(6)—C(25)—C(26) and C(5)—O(5)—C(23)—C(24) torsion angles are −165.1(5)° and −166.2(5)° (**A**) and 173.7(5)° and −174.9(5)° (**B**), respectively) and are oppositely directed.

In molecule **C**, both five-membered rings of the phthalimide substituents adopt a highly flattened envelope conformation (the C(14″) and C(22″) atoms deviate from the plane through the remaining atoms of the ring by 0.06 Å and −0.05 Å, respectively). These substituents are virtually perpendicular to the plane of the aromatic ring (the C(1″)—C(2″)—N(1″)—C(7″) and C(1″)—C(6″)—N(2″)—C(22″) torsion angles are 112.1(6)° and 81.9(7)°, respectively).

The orientations of the ether substituents in molecule **C** with respect to the plane of the benzene ring are substantially different. One substituent (at the C(5″) atom) is in an eclipsed conformation (the C(4″)—C(5″)—O(5″)—C(23″) torsion angle is −7.6(8)°), while the second substituent is noticeably rotated (the C(4″)—C(3″)—O(6″)—C(25″) torsion angle is −39.8(8)°). As in the case of molecule **A**, the O(5″) and O(6″) atoms of the ether substituents in molecule **C** deviate from the plane of the benzene ring by −0.13 Å and −0.08 Å, respectively.

Unlike molecules **A** and **B**, the trifluoromethyl groups in molecule **C** are in different orientations with respect to the O—C(Ar) bond. One group is in the *ap* conformation (the C(5″)—O(5″)—C(23″)—C(24″) torsion angle is −160.0(9)°), while the second group is in the +*ac* conformation (the C(3″)—O(6″)—C(25″)—C(26″) tor-

**Table 5.** Bond lengths in the structure of **2** averaged over three symmetrically independent molecules

| Bond | *d*/Å | Bond | *d*/Å | Bond | *d*/Å | Bond | *d*/Å | Bond | *d*/Å |
|---|---|---|---|---|---|---|---|---|---|
| N(1)—C(7) | 1.404 | O(5)—C(23) | 1.400 | C(8)—C(13) | 1.382 | C(18)—C(19) | 1.371 | C(26)—F(6) | 1.314 |
| N(1)—C(14) | 1.404 | O(6)—C(3) | 1.363 | C(9)—C(10) | 1.39 | C(19)—C(20) | 1.383 | C(26)—F(5) | 1.334 |
| N(1)—C(2) | 1.421 | O(6)—C(25) | 1.417 | C(10)—C(11) | 1.38 | C(20)—C(21) | 1.393 | O(1S)—C(3S) | 1.364(9) |
| N(2)—C(15) | 1.406 | C(1)—C(6) | 1.373 | C(11)—C(12) | 1.382 | C(21)—C(22) | 1.494 | O(1S)—C(1S) | 1.390(9) |
| N(2)—C(22) | 1.399 | C(1)—C(2) | 1.383 | C(12)—C(13) | 1.385 | C(23)—C(24) | 1.466 | O(2S)—C(2S) | 1.379(8) |
| N(2)—C(6) | 1.424 | C(2)—C(3) | 1.400 | C(13)—C(14) | 1.452 | C(24)—F(3) | 1.319 | O(2S)—C(5S) | 1.383(8) |
| O(1)—C(7) | 1.211 | C(3)—C(4) | 1.381 | C(15)—C(16) | 1.481 | C(24)—F(1) | 1.293 | C(1S)—C(2S) | 1.554(9) |
| O(2)—C(14) | 1.221 | C(4)—C(5) | 1.387 | C(16)—C(17) | 1.365 | C(24)—F(2) | 1.320 | C(3S)—C(4S') | 1.455(9) |
| O(3)—C(15) | 1.204 | C(5)—C(6) | 1.392 | C(16)—C(21) | 1.382 | C(25)—C(26) | 1.489 | C(3S)—C(4S) | 1.516(9) |
| O(4)—C(22) | 1.205 | C(7)—C(8) | 1.475 | C(17)—C(18) | 1.395 | C(26)—F(4) | 1.311 | C(5S)—C(6S) | 1.521(8) |
| O(5)—C(5) | 1.367 | C(8)—C(9) | 1.381 | | | | | | |

**Table 6.** Bond angles in the structure of **2** averaged over three symmetrically independent molecules

| Angle | ω/deg | Angle | ω/deg | Angle | ω/deg | Angle | ω/deg |
|---|---|---|---|---|---|---|---|
| C(7)—N(1)—C(14) | 110.1 | C(1)—C(6)—C(5) | 119.7 | O(3)—C(15)—N(2) | 124.9 | F(1)—C(24)—F(2) | 103.8 |
| C(7)—N(1)—C(2) | 124.5 | C(1)—C(6)—N(2) | 120.4 | O(3)—C(15)—C(16) | 129.5 | F(3)—C(24)—C(23) | 111.7 |
| C(14)—N(1)—C(2) | 124.9 | C(5)—C(6)—N(2) | 119.8 | N(2)—C(15)—C(16) | 105.6 | F(1)—C(24)—C(23) | 113.7 |
| C(15)—N(2)—C(22) | 112.1 | O(1)—C(7)—N(1) | 124.8 | C(17)—C(16)—C(21) | 120.9 | F(2)—C(24)—C(23) | 111.4 |
| C(15)—N(2)—C(6) | 124.3 | O(1)—C(7)—C(8) | 129.2 | C(17)—C(16)—C(15) | 130.7 | O(6)—C(25)—C(26) | 108.5 |
| C(22)—N(2)—C(6) | 122.3 | N(1)—C(7)—C(8) | 106.0 | C(21)—C(16)—C(15) | 108.4 | F(4)—C(26)—F(6) | 108.0 |
| C(5)—O(5)—C(23) | 118.8 | C(9)—C(8)—C(13) | 121.3 | C(16)—C(17)—C(18) | 117.4 | F(4)—C(26)—F(5) | 107.1 |
| C(3)—O(6)—C(25) | 118.3 | C(9)—C(8)—C(7) | 130.2 | C(19)—C(18)—C(17) | 121.5 | F(6)—C(26)—F(5) | 105.7 |
| C(6)—C(1)—C(2) | 120.3 | C(13)—C(8)—C(7) | 108.4 | C(18)—C(19)—C(20) | 121.3 | F(4)—C(26)—C(25) | 111.6 |
| C(1)—C(2)—C(3) | 119.4 | C(8)—C(9)—C(10) | 117.4 | C(21)—C(20)—C(19) | 116.7 | F(6)—C(26)—C(25) | 111.6 |
| C(1)—C(2)—N(1) | 120.8 | C(11)—C(10)—C(9) | 120.8 | C(20)—C(21)—C(16) | 122.2 | F(5)—C(26)—C(25) | 112.5 |
| C(3)—C(2)—N(1) | 129.7 | C(10)—C(11)—C(12) | 121.9 | C(20)—C(21)—C(22) | 128.8 | C(3S)—O(1S)—C(1S) | 123(1) |
| O(6)—C(3)—C(4) | 123.8 | C(11)—C(12)—C(13) | 117.0 | C(16)—C(21)—C(22) | 109.1 | C(2S)—O(2S)—C(5S) | 108.0(9) |
| O(6)—C(3)—C(2) | 116.0 | C(8)—C(13)—C(12) | 121.5 | O(4)—C(22)—N(2) | 125.1 | O(1S)—C(1S)—C(2S) | 109(1) |
| C(4)—C(3)—C(2) | 120.1 | C(8)—C(13)—C(14) | 108.2 | O(4)—C(22)—C(21) | 130.2 | O(2S)—C(2S)—C(1S) | 107(1) |
| C(3)—C(4)—C(5) | 119.9 | C(12)—C(13)—C(14) | 130.3 | N(2)—C(22)—C(21) | 104.8 | O(1S)—C(3S)—C(4S') | 125(1) |
| O(5)—C(5)—C(4) | 124.4 | O(2)—C(14)—N(1) | 122.9 | O(5)—C(23)—C(24) | 107.7 | O(1S)—C(3S)—C(4S) | 111(1) |
| O(5)—C(5)—C(6) | 115.4 | O(2)—C(14)—C(13) | 130.0 | F(3)—C(24)—F(1) | 107.6 | C(4S')—C(3S)—C(4S) | 123(1) |
| C(4)—C(5)—C(6) | 110.2 | N(1)—C(14)—C(13) | 107.2 | F(3)—C(24)—F(2) | 108.1 | O(2S)—C(5S)—C(6S) | 104.5(9) |

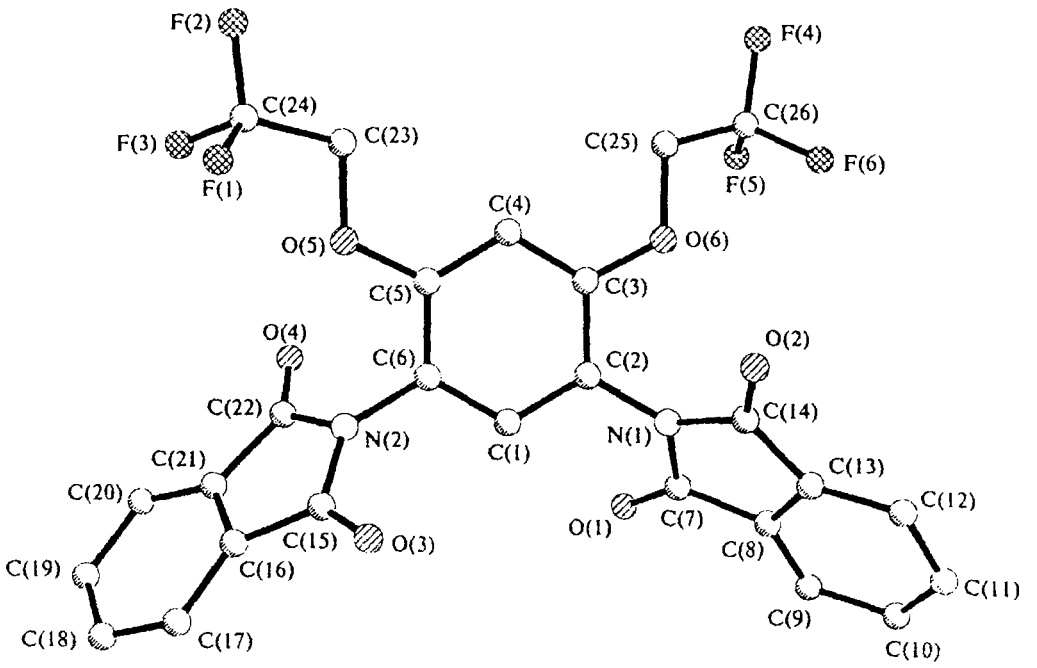


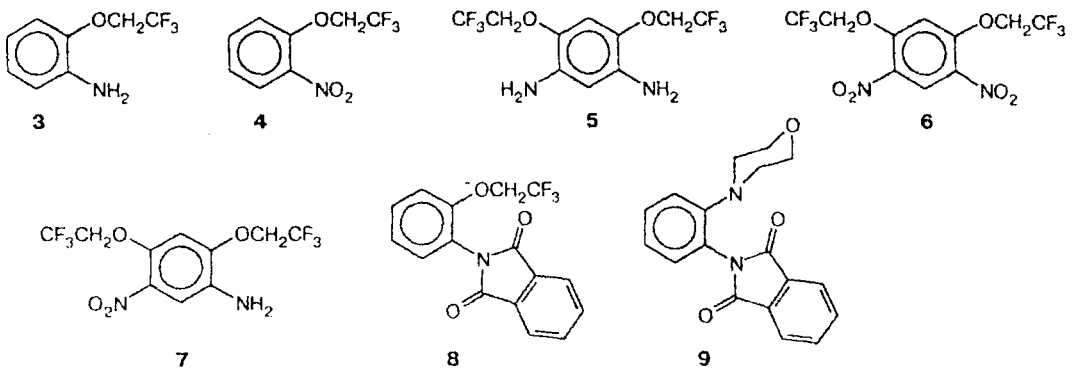

**Fig. 2.** Structure of compound **2**.

sion angle is 106.2(6)°) in spite of the presence of the shortened intramolecular contacts F(5")...H(4"A) (2.37 Å ; the sum of the van der Waals radii[8] is 2.56 Å). However, as in the case of molecules **A** and **B**, the $CF_3$ groups are oppositely directed.

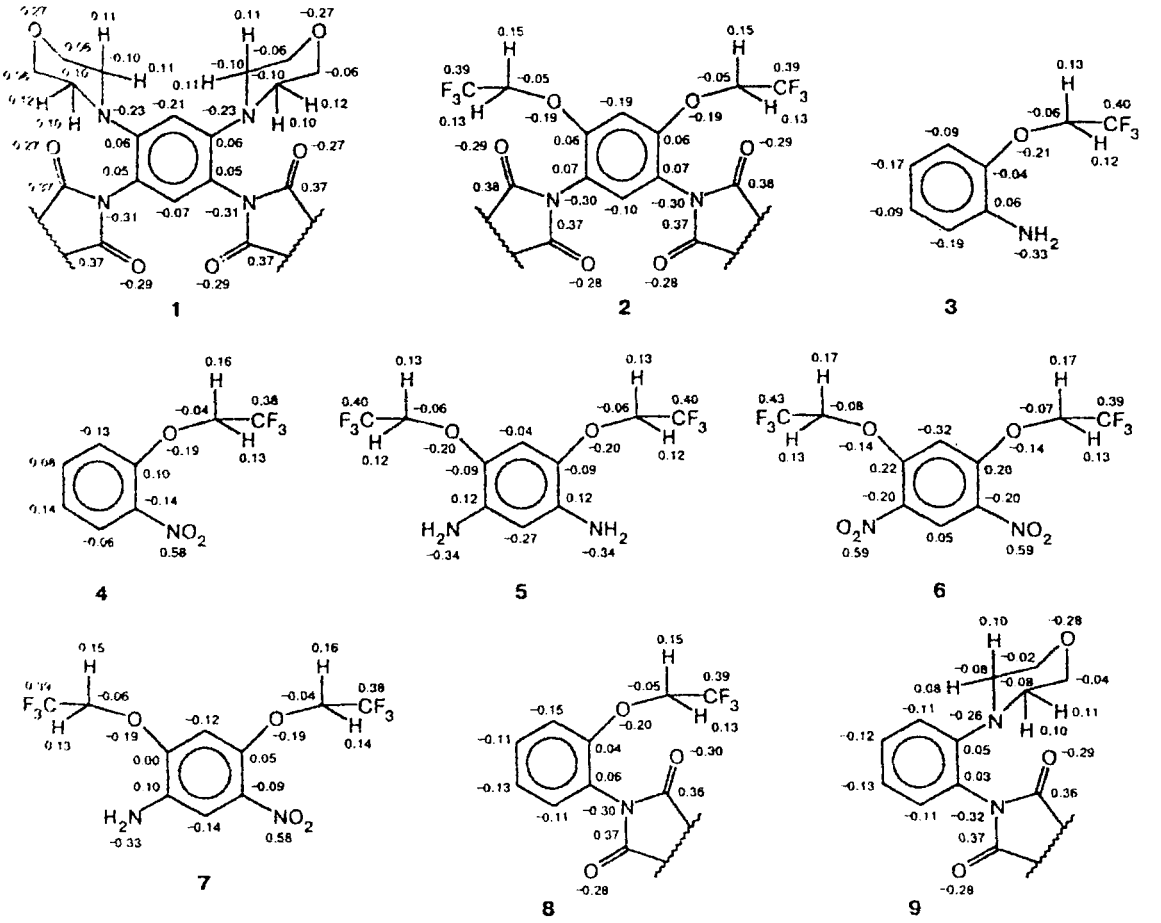
The calculations of the equilibrium geometry of compound **2** demonstrated that the bond lengths, bond angles, and torsion angles agree well with the experimental values, except for the orientation of the trifluoroethyl substituents, which adopt, according to the results of calculations, the *+sc* and *−ac* conformations.

In the crystal, molecules **2** are linked in a three-dimensional framework *via* the shortened intermolecular contacts O(2')...H(23B) (1 − *x*, −2 − *y*, −*z*) (2.37 Å; the sum of the van der Waals radii[8] is 2.45 Å), O(2")...H(23E) (2 − *x*, −1 − *y*, 1 − *z*) (2.31 Å ), O(1')...H(1"A) (*x*, *y* − 1, *z* − 1) (2.35 Å), O(4')...H(25D) (1 − *x*, −2 − *y*, −1 − *z*) (2.14 Å ), and C(22)...H(17"C) (*x*, *y* − 1, *z* − 1) (2.83 Å; the sum of the van der Waals radii[8] is 2.87 Å ).

Benzene derivatives that contain alkylamine, amide, and other groups at the *ortho* positions attract particular attention because they are starting compounds for preparing heteropolymers both by intra- and intermolecular condensation with the participation of the hydrogen atoms of the alkylamine substituents and of the carbonyl groups of the amide fragments. To carry out these transformations, knowledge of the charge distribution over the atoms of the reacting groups, in particular, of the values of the positive charges on the hydrogen atoms at the β positions of the ether groups as well as of the charges on the carbonyl groups in the amide substituents, is of primary importance. For this purpose, we calculated the equilibrium geometries of model compounds **1**—**9**.



**Scheme 1**



One of the most important prerequisites to the condensation reaction is the presence of the methylene group with rather "acidic" hydrogen atoms, *i.e.*, these atoms should carry substantial positive charges. The analysis of the calculated atomic charges (see Scheme 1) demonstrated that the methylene groups of the ether (compounds **2**—**8**) and morpholine (compounds **1** and **9**) substituents meet this requirement. A change in the electronic character of the substituents in the benzene ring (for example, in molecules **3**, **4**, and **5**—**7**) has no noticeable effect on the above-mentioned charges.

The simultaneous presence of the methylene and carbonyl groups in appropriate orientations in compounds **1**, **2**, **8**, and **9** may cause the reactions of intramolecular condensation to occur. In the course of the reaction, substantial flattening of the molecule should occur due to a decrease in the angles of rotation of the substituents with respect to the plane of the benzene ring. This change in the conformation of compounds **1**, **2**, **8**, and **9** may be essentially hindered due to steric repulsions between the substituents.

To estimate these effects, we calculated the geometries of the molecules under study with the fixed coplanar arrangement of the benzene ring and the phthalimide substituents and their potential energies. The differences in the energies of the flattened and equilibrium conformations are 6 and 10 kcal $mol^{-1}$ in molecules **8** and **9**, respectively, and 14 and 26 kcal $mol^{-1}$ in tetrasubstituted compounds **1** and **2**, respectively. The orientations of the ether and morpholine substituents remain virtually unchanged. Therefore, intramolecular condensation should occur more readily in ether derivatives owing to lower steric hindrances. It should be noted that the barriers to flattening in the molecules under consideration are relatively small and can be readily overcome when the reaction is carried out at high temperature.

Therefore, the results obtained demonstrated that in molecules **1**—**9** the methylene and carbonyl groups are potentially reactive in reactions of intra- and intermolecular condensation. Consequently, these compounds can be successfully used for preparing new classes of heterocyclic polymers.

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