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Anionic Spirocyclization of 3-Nitro-4-(2-hydroxyphenoxy)-2H-1-benzopyran-2-one: Formation of Stabilized Meisenheimer-type Salts

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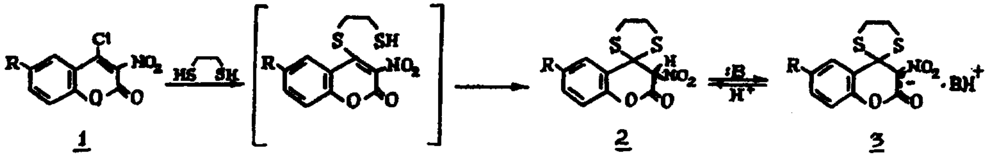
Abstract: The interaction of 3-nitro- and 3,6-dinitro-4-(2-hydroxy-4,5-R_2-phenoxy)-2H-1-benzopyran-2-ones 4a-d with triethylamine leads to the formation of triethylammonium salts of corresponding anionic spirocyclic compounds 5a-d as a result of intramolecular nucleophilic attack of aroxide-ion on position 4 of the benzopyran system. The structures are proved by ^1H NMR, IR spectroscopy and X-ray analysis of 5c. The distribution of electron density in the model anion M was calculated from X-ray data.

The interaction of bis-nucleophiles with 2H-1-benzopyran-2-ones with the leaving groups in 3 and 4 positions usually results in annelation of a new heterocycle to a lactone ring in these positions[1]. The possibility of formation of a spiro heterocycle by bis-nucleophilic attack on position 4 has been earlier postulated[2] when considering the mechanisms of some transformations, and recently[3] we have proved it by synthesis of 3-nitro-6-R-spiro(3,4-dihydro-2H-[1]-benzopyran-4,2'-[1,3]dithiolan)-2-ones 2 and the related conjugate bases 3 through the interaction of 4-chloro-3-nitro-6-R-2H-1-benzopyran-2-ones 1 with 1,2-ethanedithiol in the presence of bases (Scheme 1).

Compounds of the 3 type are of considerable interest as stable anionic intermediates in nucleophilic additions to an activated double bond C=C[4]. The precursor to anion 3 in the above example is the spiro cyclic product 2 whose easy formation is provided by high nucleophilic

Scheme 1



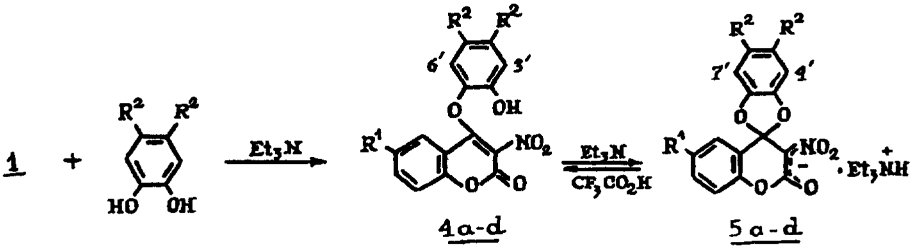
R = H, NO2

capacity of S-nucleophiles[4,5] and in terms of HSAB theory[5] by the high affinity of soft (polarized) alkene for the soft S-base and the "symbiosis" of two soft centers at one carbon atom.

In this paper we report the first example of direct anionic spiro cyclization in the 2H-1-benzopyran-2-one series, and the unambiguous X-ray confirmation of the anion structure.

The 3-nitro- and 3,6-dinitro-4-(2-hydroxyphenoxy)- and related -4-(2-hydroxy-4,5-dichlorophenoxy)-2H-1-benzopyran-2-ones 4a-d were synthesized as model compounds by condensation of 1 with catechols in the presence of triethylamine (Scheme 2).

Scheme 2



a, $R^1=R^2=H$; b, $R^1=H$, $R^2=Cl$; c, $R^1=NO_2$, $R^2=H$; d, $R^1=NO_2$, $R^2=Cl$

It turned out, however, that when we used an equimolar amount of the base, transformation of initial compounds did not exceed 50% and triethylammonium salts 5a-d were obtained as reaction products. This kind of interaction is evidence for the considerable thermodynamic stability of anions 5a-d due to conformational rigidity of a cyclized catechol fragment in 4a- -d. For example, in the similar system 1-(2-hydroxyphenoxy)-2,4,6-trinitrobenzene - anionic spiro complex[6,7], the influence of the entropy factor is so strong, that the rate constant of the spirocycle ring closure

(10^9 s^{-1}) turns out to be the highest for nucleophilic attack on the carbon atoms in aromatics, and the proton transfer under certain conditions has been found to be rate-limiting[7].

The preparation of 4a-d was achieved by using two equivalents of triethylamine with isolation of salts 5a-d followed by acidification by trifluoroacetic acid to 4a-d. It should be pointed out that compounds 4a-d are easy to hydrolyze, forming the corresponding 4-hydroxy-2H-1-benzopyran-2-ones and catechols. Thus, for example, the almost quantitative hydrolysis of 4c is observed in DMSO-d_6 in 15 min (for 4d this process is even faster). It is also observed on acidification of salts 5a-d by aqueous HCl. The mononitro-substituted 4a,b are a little more resistant to hydrolysis.

The "open" structures of 4a-d and spiro structures of 5a-d are confirmed by ^1H NMR, IR and electronic spectra (Table 1) where characteristic changes take place in the course of the interconversion of 4 and 5.

In ^1H NMR spectra 4 a broad signal is observed in the range 9-10 ppm for the OH-group proton and there is no singlet of H3 proton expected in the range 6-7 ppm for alternative spiro structures of type 2. In transition 4→5 the signals of all corresponding protons shift to higher field. The asymmetric multiplets of H3′-6′ protons in 4a,c and two singlets of H3′,6′ in 4b,d of catechol fragments turn respectively into symmetric multiplets of AA'BB' in 5a,c and into singlets in 5b,d due to the appearance of a symmetry plane in anions 5 (point group C_s). When trifluoroacetic acid is added to solutions 5a-d in an NMR cell there occurs immediate and complete transformation of the spectra of the 5 into those of the initial compounds 4a-d which indicates that the formation of 5 is reversible. Some characteristic changes also take place in the IR spectra during the transformation of 4 into 5. As opposed to spectra 4, the spectra 5 have no ν_{OH} band in the range 3300-3400 cm^{-1} and the band $\nu_{C=O}$ shifts (excluding system 4a-5a) to lower frequency. In the mononitrocompounds 4a,b, transition to anions 5a,b leads to the disappearance of the nitro groups absorptions ν_{as}(~1540 cm^{-1}) and ν_s(~1380 cm^{-1}) and the appearance of intense bands at ~1485 cm^{-1} and ~1310 cm^{-1}, which may be assigned respectively to ν_{as} and ν_s of the nitro group bearing a partial negative charge[8]. Besides, intense bands in the range 1230-1270 cm^{-1} appeare in the spectra of 5a,b. These bands are assigned to the stretching vibrations C_{Ar}-O of the 1,3-benzodioxolan ring. Changes of this kind also take place in the dinitro cases 4c,d-5c,d. Besides, in the spectra of 4c,d antisymmetric stretching vibrations of the nitro group in position 6 at 1535 and 1530 cm^{-1} are observed. These bands retain

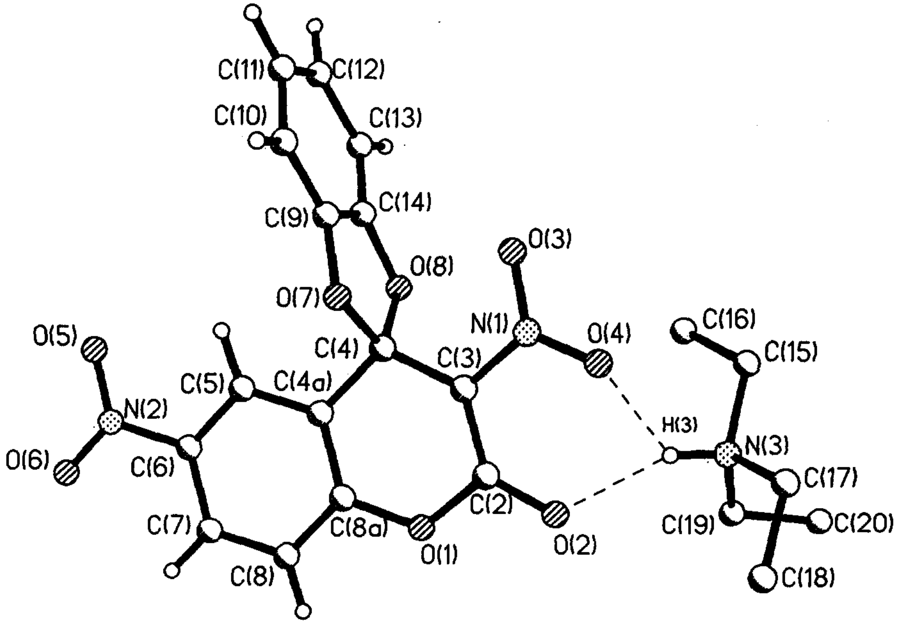


Figure 1. A perspective view of ionic pair in structure 5c (H-atoms of Et-groups of cation omitted for clarity)

their position in the anions 5c,d. There is one more band at 1570 cm^{-1} in spectra of 4a-d which disappears in spectra of 5a-d. This band, of medium intensity, is also observed in the spectra of model compounds such as 3-nitro-(4e) and 3,6-dinitro-4-phenoxy-2H-1-benzopyran-2-ones (4f) and it is probably a stretching vibration of the double bond C3=C4. The specific character of the changes in the IR spectra of 4 and 5 indicates that both the carbonyl and the nitro group in position 3 participate in delocalization of the negative charge in the anion 5.

The electronic spectra of 5 show a shift of absorption to the long-wave region and an increase in their intensity, compared with the spectra of 4.

To prove unambiguously the spiro structure of anion 5 we undertook an X-ray study of the triethylammonium salt 5c. The geometrical parameters for 5c are listed in Tables 2 and 3 (according to the numbering system for atoms in molecular structure shown in Fig.1). In the crystal of 5c the anion and cation Et_3NH^+ are linked by a bifurcated H-bond N-H...O with participation of oxygen O(2) and O(4) atoms. The bond lengths of N(1)-O(3) and N(1)-O(4) in a nitro group at atom C(3) are longer than the bonds N-O in the nitro group at C(6), and the bond N(1)-C(3) is shortened relative to bond N(2)-C(6). There is a considerable decrease in the bond length C(2)-C(3) (1.413Å) as compared with that found, for example, in 4,4,5,7,8-pentamethyl-3,4-dihydro-2H-1-benzopyran-2-one[9] (1.505Å), while bond C(2)-O(2) is somewhat longer (1.217 and 1.199Å respectively).

The atoms of the benzopyran system are planar (accuracy within 0.033Å). The nitro groups at C(3) and C(6) are rotated relative to the benzopyran plane through 11.2° and 2.0° respectively. The planes of the spiro fragments are almost orthogonal; the dihedral angle between them is 91.3°. Other geometrical parameters of ionic pair are normal.

The formation in structure of 5c of a bifurcated H-bond, the peculiarities in the geometry of the benzopyranyl system and in the variations in the IR spectra of 4 and 5 are caused by a negative charge which is most probably delocalized in the fragment O(1)-C(2)-O(2)-C(3)-N(1)-O(3)-O(4). In an effort to analyze the distribution of electron density we have investigated the electronic structure of model anion **M** that simulates the structure of anion 5c where a catechol fragment has been replaced by two hydroxyl groups O(7)-H(9) and O(8)-H(10) for simplicity of calculation. Calculations were conducted by the MNDO technique[10]. A version of the MNDO/HB program for EC computer elaborated in ref.[11] was used. It was assumed that the benzopyran system is planar, and its geometrical parameters were taken from those listed in Table 3. Bond angles of C(4)-O(7)-H(9) and C(4)-O(8)-H(10) were taken as 106.6°, bond lengths O-H as 0.95Å, and torsion angles of N(1)-C(3)-C(4)-O as ±60°. Considering that one of the contributing structures of anion 5 has a fragment C(2)-O(2)$^-$, we varied the length of this bond starting from the single bond length C-O 1.41Å. The optimal C(2)-O(2) bond length was found to be 1.229Å which is close to the experimental value of 1.217Å. The effective charge values are given in Table 4.

The resulting figure show that the charge -1.04 a.u. is concentrated in the fragment O(2)-C(2)-C(3)-N(1)-O(3)-O(4) and it is unevenly distributed over the atoms, showing considerably alternation. Effective charges in atoms C(3) and N(1) are of opposite sign and their absolute values are nearly equal. Similar picture is observed to bonds C(2)-O(2) and C(2)-C(3), but absolute values of two alternative charges differ by 0.1 a.u. Such distribution of effective charges close to their distribution in dipoles may bring about shortening of bonds N(1)-C(3), C(2)-C(3) and C(2)-O(2) mentioned above. Large and similar charges in atoms O(4) and O(2) (-0.43 and -0.34 respectively) favour formation of the bifurcated H-bond and leads to a lengthening of bonds N(1)-O(3) and N(1)-O(4). The overall negative charge in nitro group N(1)-O(3)-O(4) is 0.07 a.u. greater than that on nitro group N(2)-O(5)-O(6).

The HOMO analysis indicates that this is a π-orbital and that the greatest contribution in this orbital is made by C(3) atom (coefficient for $2p_z$ AO is 0.82). Oxygen atoms O(2), O(3) and O(4) also participate in distribution of electron density of this MO (coefficients for $2p_z$ AO are 0.35, 0.30 and 0.26 respectively). Contributions of other atoms are small. Consequently the charge of an additional electron that occupies HOMO is actually delocalized in these four atoms and about 60% of electron density is concentrated in atom C(3).

The calculated Wiberg indices W(X-Y) adequately reflect trends towards changes in bond lengths in 5c. Thus the Wiberg indices for bonds N-O in the nitro group at atom C(6) are 1.420 (N(2)-O(6)) and 1.444 (N(2)-O(5)), while for longer bonds of N(1)-O(3) and N(1)-O(4) in the nitro group at atom C(3) these values are not so large (1.373 and 1.354 respectively). Similar relations are observed in bonds N(2)-C(6) and N(1)-C(3) and the W(X-Y) indices are 0.892 and 1.052.

And, finally, we may presume on the basis of the calculation that protonation of anion 5 (process 5→4, scheme 2) is not a result of a direct attack of a proton on one of the oxygen atoms of the 1,3-benzodioxolan ring (possibly a concerted process closely resembling the one shown in ref.[12]) but it results from attachment of a proton to atom C(3) carrying the largest negative charge with formation of an intermediate of type 2 (Scheme 1) which subsequently forms 4 by intra- or intermolecular routes. Transformation of the intermediate of types 2 to 4 may be too rapid to be recorded by usual spectroscopic technique. Data that confirm this assumption have been obtained in a similar example and will be published.

EXPERIMENTAL SECTION

^1H NMR spectra were recorded on the Bruker AC 250 MHz spectrometer, IR spectra (KBr pellets) on the Perkin-Elmer 577 and electron spectra on the Specord M40 spectrometer. The reaction processes were controlled by using TLS (Silufol UV-254, benzene/acetone:8/1).

X-ray crystal structure analysis of 5c. $C_{21}H_{23}N_3O_8$, F.W.=445.4; monoclinic, space group $P2_1/n$; at -90°C a=8.398(2), b=9.334(2), c=26.750(5) Å, β=93.30(3)°, V=2093.3(8)Å^3, Z=4, D_x=1.41 g/cm^3, μ(Mo-Kα)=0.103 mm^{-1}. Intensity of 2993 independent reflections with $I \geq 2\sigma(I)$ were measured on Siemens P3/PC diffractometer (monochromatized Mo-Kα radiation, $\theta/2\theta$-scan, $2\theta \leq 60^\circ$, $-90^\circ C$). The structure was solved by direct method (no absorption correction) and was refined anisotropically for all non-hydrogen atoms by full-matrix least-squares procedure. All H atoms were located from difference map and refined isotropically. The structure was refined to R=0.044, R_W=0.045. All calculation were performed on IBM PC/AT computer with using SHELXTL PC programs. Non-hydrogen coordinates are listed in Table 5, hydrogen atom coordinates in Table 6.

Preparation of 5a-d (general procedure). A solution of corresponding catechol (1 mmol) and triethylamine (2 mmol) in 3 ml of benzene gradually added to a stirred solution of the corresponding 4-chloro-3-nitro-6-R-2H-1-benzopyran-2-one[13] (1 mmol) and stirred for 1.5 h. The precipitate was filtered and washed with benzene and water. The product was dried in vacuo over P_2O_5.

Preparation of4a-d (general procedure). A solution of 4 mmol CF_3COOH in 5 ml benzene gradually added to a stirred suspension of 1 mmol of 5a-d in 15 ml of benzene. The solvent was removed under reduced pressure on a rotatory evaporator and the residue was treated with water. The crystalline residue was filtered off, washed with water, and dried in vacuo over P_2O_5.

Preparation of 3,6-dinitro-4-phenoxy-2H-1-benzopyran-2-one (4f). The procedure is similar to that for 5a-d but in this case 1 mmol of triethylamine was used.

Preparation of 3-nitro-4-phenoxy-2H-1-benzopyran-2-one (4a). A solution of 1.1 mmol of phenol and 1.1 mmol of triethylamine in 3 ml of benzene added to a solution of 1 mmol of 4-chloro-3-nitro-2H-1-benzopyran-2-one in 10 ml benzene and stirred for 1 h. The reaction mixture was washed with water, dried with $MgSO_4$, the solvent was removed under reduced pressure on a rotatory evaporator and the residue was dried in vacuo.

Table 1. Yields, Physical and Spectral Data of Products

Product	Yield(%), mp(°C), Solvent for Crystallization	IR(KBr, cm^{-1}), ^1H NMR(δ, acetone-d_6, TMS, J Hz), UV (CH_3CN, nm, lg ε), Microanalysis
4a	67, 184-185 ethylace- tate -	νOH, 3320; νC=O, 1690; $\nu_{as}NO_2$, 1542; ν_sNO_2, 1382; νC3=C4, 1565 ^1H: 8.08(dd, 1H, H5); 7.87 (ddd, 1H, H7); 7.52 (dd, 1H, H8); 7.52 (ddd, 1H, H6); 7.24 (dd, 1H, H6'); 7.14

	hexane, 1:1	(ddd, 1H, H4'); 7.02 (dd, 1H,H3'); 6.84 (ddd,1H, H5'); $J_{5,6}$ 8.2; $J_{5,7}$ 1.6; $J_{6,7}$ 7.3; $J_{6,8}$ 1.1; $J_{7,8}$ 8.4; $J_{3',4'}$ 8.1; $J_{3',5'}$ 1.6; $J_{4',5'}$ 7.4; $J_{4',6'}$ 1.5; $J_{5',6'}$ 8.1 λ_{max}: 276 (3.94); 312 sh (3.63) Calcd for $C_{15}H_9NO_6$; C, 60.21; H, 3.03. Found: C, 60.56; H, 3.06
4b	61, 195-197, (decomp.), ethylacetate - hexane, 1:2	νOH, 3280; νC=O, 1708; $\nu_{as}NO_2$, 1538; $\nu_{s}NO_2$, 1383; νC3=C4, 1570 ^{1}H: 8.04 (dd, 1H, H5); 7.89 (ddd, 1H, H7); 7.56 (dd, 1H, H8); 7.54 (ddd, 1H, H6); 7.58 (s, 1H, H6'); 7.22 (s, 1H, H3'); $J_{5,6}$ 8.0; $J_{5,7}$ 1.6; $J_{6,7}$ 7.3; $J_{6,8}$ 1.1; $J_{7,8}$ 8.2. λ_{max}: 282 (4.10), 311 sh (3.85) Calcd for $C_{15}H_7Cl_2NO_6$: C, 48.94; H, 1.92; N, 3.80. Found: C, 48.69; H, 1.78; N, 3.96.
4c	59, 244-246, (decomp.) ethylacetate	νOH, 3385; νC=O, 1750; $\nu_{as}NO_2$3, 1545; $\nu_{as}NO_2$6, 1535; $\nu_{s}NO_2$3, 1378; $\nu_{s}NO_2$6, 1350; νC3=C4, 1577 ^{1}H: 8.96 (dd, 1H, H5); 8.69 (dd, 1H, H7); 7.81 (dd, 1H, H8); 7.29 (dd, 1H, H6'); 7.18 (ddd, 1H, H4'); 7.03 (dd, 1H, H3'); 6.88 (ddd, 1H, H5'); $J_{5,7}$ 2.7; $J_{5,8}$ 0.3; $J_{7,8}$ 9.2; $J_{3',4'}$ 8.2; $J_{3',5'}$ 1.5; $J_{4',5'}$ 7.4; $J_{4',6'}$ 1.6; $J_{5',6'}$ 8.1 λ_{max}: 260 (4.46); 312 sh (3.85) Calcd for $C_{15}H_8N_2O_8$: C, 52.33; H, 2.34 Found: C, 52.41; H, 2.35
4d	34, 194-195, (decomp.), ethylacetate - hexane, 1:1	νOH, 3410; νC=O, 1760; $\nu_{as}NO_2$3, 1550; $\nu_{as}NO_2$6, 1530; $\nu_{s}NO_2$3, 1385; $\nu_{s}NO_2$6, 1355; νC3=C4, 1577 ^{1}H: 8.94 (d, 1H, H5); 8,70 (dd, 1H, H7); 7.82 (d, 1H, H8); 7.61 (s, 1H, H6'); 7.24 (s, 1H, H3'); $J_{5,7}$ 2.7; $J_{7,8}$ 9.2 λ_{max}: 260 (4.42); 312 sh (3.81) Calcd for $C_{15}H_6Cl_2N_2O_8$: C, 43.61; H, 1.46; N, 6.78. Found: C, 44.34, H, 1.64; N, 6.65
4e	80, 135-137, CCl_4	νC=O, 1750; $\nu_{as}NO_2$, 1523; $\nu_{s}NO_2$, 1380; νC3=C4, 1566. ^{1}H: 7.87 (dd, 1H, H5); 7.87 (ddd, 1H, H7); 7.55 (dd, 1H, H8); 7.47 (ddd, 1H, H6); 7.25-7.47 (m, 5H, Ph); $J_{5,6}$ 7.9; $J_{5,7}$ 1.7; $J_{6,7}$ 7.4; $J_{6,8}$ 1.1; $J_{7,8}$ 7.9 Calcd for $C_{15}H_9NO_5$: C, 63.60; H, 3.20; N, 4.95. Found: C, 63,49; H, 3.15; N, 5.13

4f	67, ethylacetate - hexane, 1:1	νC=O, 1750; ν_{as}NO$_2$, 1537 (broad); ν_sNO$_2$3, 1380; ν_sNO$_2$6 1353; νC3=C4, 1573 ^{1}H: 8.79 (dd, 1H, H5); 8.68 (dd, 1H, H7); 7.82 (dd,1H, H8); 7.30-7.50 (m 5H, Ph); $J_{5,7}$ 2.7; $J_{7,8}$ 9.1; $J_{5,8}$ 0.3 Calcd for $C_{15}H_8N_2O_7$: C, 54.89; H, 2,46; N, 8.53 Found: C, 54.86; H, 2.49; N, 8.90
5a	69, 143-144, (decomp.), ethylacetate	νC=O, 1688; ν_{as}NO$_2^-$, 1485; ν_sNO$_2^-$, 1300 ^{1}H: 7.47 (dd, 1H, H5); 7.43 (ddd, 1H, H7); 7.13 (ddd, 1H, H6); 7.05 (dd, 1H, H8); $J_{5,6}$ 7.8; $J_{5,7}$ 1.6; $J_{6,7}$ 7.4; $J_{6,8}$ 1.2; $J_{7,8}$ 8.2; 6.74 (symm. m, 4H, H4'-H7'); 6.78 (H4', H7'); 6.70 (H5',H6'); $J_{4',5'}=J_{5',6'}=J_{6',7'}=$ $=7.7$; $J_{4',6'}=J_{5',7'}=1.3$; $J_{4',7'}$ 0.3 (program PANIC) λ_{max}: 285 (4.01); 317 (4.11) Calcd for $C_{21}H_{24}N_2O_6$: C, 62.99; H, 6.04; N, 7.00 Found: C, 62.82; H, 6.05; N, 6.99
5b	50, 168-170, (decomp.), ethylacetate	νC=O, 1660; ν_{as}NO$_2^-$, 1485; ν_sNO$_2^-$, 1310 ^{1}H:7.47 (dd,1H,H5); 7.46 (ddd, 1H, H7); 7.17 (ddd, 1H, H6); 7.06 (dd, 1H, H8); 6.88 (s, 2H, H4', H7'); $J_{5,6}$ 7.8; $J_{5,7}$ 1.6; $J_{6,7}$ 7.3; $J_{6,8}$ 1.1; $J_{7,8}$ 8.0 λ_{max}: 305 (4.20); 317 sh (4.13) Calcd for $C_{21}H_{22}Cl_2N_2O_6$: C, 53.73; H, 4.52; N, 6.03 Found: C, 53.97; H, 4.62; N, 6.44
5c	74, 176-179, (decomp.), acetonitrile	νC=O, 1677; ν_{as}NO$_2^-$3, 1482; ν_{as}NO$_2$6, 1538; ν_sNO$_2^-$3, 1315; ν_s NO$_2$6, 1350 ^{1}H: 8.32 (d, 1H, H5); 8.30 (dd, 1H, H7); 7.29 (d, 1H, H8); $J_{5,7}$ 2.7; $J_{7,8}$ 9.1; 6.80 (symm. m, 4H, H4'-H7'): 6.84 (H4', H7'); 6.76 (H5',H6'); $J_{4',5'}=J_{5',6'}=J_{6',7'}=$ $=7.7$; $J_{4',6'}=J_{5',7'}=1.2$; $J_{4',7'}$ 0.3 (program PANIC) λ_{max}: 285 (4.15); 317 (4.27) Calcd for $C_{21}H_{23}N_3O_8$: C, 56.63; H, 5.20; N, 9.43 Found: C, 56.63; H, 5.24; N, 9.25.
5d	65, 179-181, (decomp.) acetonitrile	νC=O, 1695; ν_{as}NO$_2^-$3, 1487; ν_{as}NO$_2$6, 1533; ν_sNO$_2^-$3, 1305; ν_sNO$_2$6, 1358 ^{1}H: 8.28 (d, 1H, H5); 8.33 (dd, 1H, H7); 7.32 (d, 1H, H8); 6.98 (s, 2H, H4', H7'); $J_{5,7}$ 2.7; $J_{7,8}$ 9.0 λ_{max}: 306 (4.31); 316 sh (4.28) Calcd for $C_{21}H_{21}Cl_2N_3O_8$: C, 49.03; H, 4.12; N, 8.17. Found: C, 48.97; H, 4.06; N, 8.25

Table 2. Bond Lengths, d (Å), of Structure 5c

Bond	d	Bond	d	Bond	d
O(1)-C(2)	1.400(3)	N(3)-C(15)	1.507(3)	C(9)-C(14)	1.382(3)
O(1)-C(8a)	1.368(3)	N(3)-C(17)	1.509(4)	C(10)-C(11)	1.403(4)
O(2)-C(2)	1.217(3)	N(3)-C(19)	1.503(3)	C(11)-C(12)	1.376(4)
O(3)-N(1)	1.248(3)	C(2)-C(3)	1.413(3)	C(12)-C(13)	1.405(4)
O(4)-N(1)	1.251(3)	C(3)-C(4)	1.478(3)	C(13)-C(14)	1.375(4)
O(5)-N(2)	1.225(3)	C(4)-C(4a)	1.505(3)	C(15)-C(16)	1.506(4)
O(6)-N(2)	1.229(3)	C(4a)-C(5)	1.390(3)	C(17)-C(18)	1.505(4)
O(7)-C(4)	1.466(3)	C(4a)-C(8a)	1.387(3)	C(19)-C(20)	1.511(5)
O(7)-C(9)	1.381(3)	C(5)-C(6)	1.383(3)	N(3)...O(2)	2.832(3)
O(8)-C(4)	1.471(3)	C(6)-C(7)	1.388(4)	N(3)...O(4)	2.939(3)
O(8)-C(14)	1.377(3)	C(7)-C(8)	1.374(4)	O(2)...H(3)	1.98(1)
N(1)-C(3)	1.406(3)	C(8)-C(8a)	1.389(3)	O(4)...H(3)	2.26(1)
N(2)-C(6)	1.465(3)	C(9)-C(10)	1.374(3)		

Table 3. Bond Angles, ω (°), of Structure 5c

Angle	ω	Angle	ω
C(2)-O(1)-C(8a)	122.2(2)	C(4)-C(4a)-C(8a)	121.3(2)
C(4)-O(7)-C(9)	107.2(2)	C(5)-C(4a)-C(8a)	118.6(2)
C(4)-O(8)-C(14)	107.0(2)	C(4a)-C(5)-C(6)	118.9(2)
O(3)-N(1)-O(4)	120.4(2)	N(2)-C(6)-C(5)	118.9(2)
O(3)-N(1)-C(3)	118.3(2)	N(2)-C(6)-C(7)	118.7(2)
O(4)-N(1)-C(3)	121.2(2)	C(5)-C(6)-C(7)	122.5(2)
O(5)-N(2)-O(6)	123.0(2)	C(6)-C(7)-C(8)	118.5(2)
O(5)-N(2)-C(6)	118.7(2)	C(7)-C(8)-C(8a)	119.6(2)
O(6)-N(2)-C(6)	118.3(2)	O(1)-C(8a)-C(4a)	122.2(2)
C(15)-N(3)-C(17)	109.6(2)	O(1)-C(8a)-C(8)	115.9(2)
C(15)-N(3)-C(19)	113.8(2)	C(4a)-C(8a)-C(8)	121.9(2)
C(17)-N(3)-C(19)	113.7(2)	O(7)-C(9)-C(10)	127.6(2)
O(1)-C(2)-O(2)	112.9(2)	O(7)-C(9)-C(14)	110.0(2)
O(1)-C(2)-C(3)	117.1(2)	C(10)-C(9)-C(14)	122.3(2)
O(2)-C(2)-C(3)	130.0(2)	C(9)-C(10)-C(11)	116.0(2)
N(1)-C(3)-C(2)	118.6(2)	C(10)-C(11)-C(12)	121.6(3)
N(1)-C(3)-C(4)	116.5(2)	C(11)-C(12)-C(13)	121.9(3)
C(2)-C(3)-C(4)	124.9(2)	C(12)-C(13)-C(14)	115.7(3)
O(7)-C(4)-O(8)	105.3(2)	O(8)-C(14)-C(9)	110.3(2)

O(7)-C(4)-C(3)	111.7(2)	O(8)-C(14)-C(13)	127.3(2)
O(8)-C(4)-C(3)	112.6(2)	C(9)-C(14)-C(13)	122.4(2)
O(7)-C(4)-C(4a)	107.4(2)	N(3)-C(15)-C(16)	112.4(2)
O(8)-C(4)-C(4a)	108.1(2)	N(3)-C(17)-C(18)	112.8(2)
C(3)-C(4)-C(4a)	111.4(2)	N(3)-C(19)-C(20)	113.7(3)
C(4)-C(4a)-C(5)	120.1(2)		

Table 4. A Distribution of Effective Charges q_x (a.u.) in the Model Structure <u>M</u>

Atom	q_x	Atom	q_x	Atom	q_x	Atom	q_x
O(1)	-0.28	O(4)	-0.43	C(8)	-0.14	O(6)	-0.35
C(2)	0.44	C(4)	0.42	C(7)	0.05	H(5)	0.11
O(2)	-0.34	O(7)	-0.29	C(6)	-0.17	H(7)	0.08
C(3)	-0.55	O(8)	-0.29	C(5)	0.11	H(8)	0.08
N(1)	0.54	C(4a)	-0.25	N(2)	0.49	H(9)	0.16
O(3)	-0.42	C(8a)	0.24	O(5)	-0.38	H(10)	0.16

Table 5. Atomic Coordinates (x10^4) and Temperature Factors U^* ($Å^2$x10^4) of Non-Hydrogen Atoms of Structure <u>5c</u>

Atom	X	Y	Z	U	Atom	X	Y	Z	U
O(1)	1742(2)	4363(2)	470(1)	335(6)	C(6)	4933(3)	7469(3)	126(1)	280(7)
O(2)	708(2)	2740(2)	941(1)	376(6)	C(7)	3675(3)	7132(3)	-213(1)	313(8)
O(3)	3979(2)	3706(2)	2096(1)	331(6)	C(8)	2611(3)	6096(3)	-84(1)	331(8)
O(4)	1659(2)	2767(2)	1908(1)	385(6)	C(8a)	2818(3)	5417(3)	378(1)	265(7)
O(5)	7227(3)	8817(3)	278(1)	527(8)	C(9)	5860(3)	6180(3)	1826(1)	254(7)
O(6)	5906(3)	9110(2)	-430(1)	498(7)	C(10)	6502(3)	7067(3)	2194(1)	347(8)
O(7)	4334(2)	6213(2)	1605(1)	256(5)	C(11)	8104(4)	6818(3)	2347(1)	417(9)
O(8)	5788(2)	4351(2)	1269(1)	255(5)	C(12)	8971(3)	5744(3)	2138(1)	425(9)
N(1)	2834(2)	3485(2)	1787(1)	272(6)	C(13)	8296(3)	4830(3)	1766(1)	345(8)
N(2)	6102(3)	8536(2)	-18(1)	355(7)	C(14)	6724(3)	5089(3)	1621(1)	265(7)
N(3)	745(2)	39(2)	1424(1)	289(6)	C(15)	2115(3)	-484(3)	1764(1)	374(9)
C(2)	1736(3)	3656(3)	931(1)	276(7)	C(16)	3709(3)	-218(3)	1550(1)	400(9)
C(3)	2891(3)	4086(3)	1306(1)	243(7)	C(17)	-768(3)	30(3)	1702(1)	399(9)
C(4)	4230(3)	5073(2)	1227(1)	220(7)	C(18)	-2161(4)	678(4)	1403(1)	491(9)
C(4a)	4052(3)	5781(2)	721(1)	227(7)	C(19)	594(3)	-719(3)	927(1)	357(9)
C(5)	5133(3)	6824(3)	591(1)	262(7)	C(20)	188(5)	-2290(4)	967(2)	523(9)

*Equivalent isotropic U defined as one third of trace of the orthogonalized U(i,j) tensor

Table 6. Coordinates (x10^3) and Isotropic Temperature Factors B (x10^3) of H Atoms of Structure 5c

Atom	X	Y	Z	B	Atom	X	Y	Z	B
H(3)	91(3)	100(3)	137(1)	37(7)	H(163)	386(3)	-82(3)	126(1)	38(8)
H(5)	603(3)	715(3)	81(1)	31(7)	H(171)	-47(4)	65(4)	203(1)	59(10)
H(7)	352(3)	761(3)	-54(1)	41(8)	H(172)	-98(3)	-97(3)	180(1)	44(8)
H(8)	174(3)	583(3)	-30(1)	33(7)	H(181)	-255(4)	5(4)	111(1)	65(10)
H(10)	583(3)	782(3)	235(1)	46(8)	H(182)	-192(4)	164(4)	124(1)	72(12)
H(11)	864(3)	742(3)	261(1)	46(8)	H(183)	-299(4)	91(4)	161(1)	68(11)
H(12)	1006(3)	564(3)	226(1)	48(9)	H(191)	-22(3)	-18(3)	72(1)	33(7)
H(13)	890(3)	403(3)	163(1)	39(8)	H(192)	156(3)	-55(3)	77(1)	41(8)
H(151)	202(3)	4(3)	208(1)	43(8)	H(201)	2(5)	-260(4)	60(2)	85(13)
H(152)	189(3)	-150(3)	185(1)	45(8)	H(202)	-87(5)	-243(4)	113(1)	74(12)
H(161)	455(4)	-43(4)	182(1)	73(9)	H(203)	102(5)	-285(4)	113(1)	81(13)
H(162)	382(3)	78(3)	142(1)	44(8)					

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