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The Crystal and Molecular Structure of the Complexes of 2,4,6-Trinitrophenetole with Caesium or Potassium Ethoxide (Meisenheimer Salts)

BY RICCARDO DESTRO, CARLO MARIA GRAMACCIOLI AND MASSIMO SIMONETTA

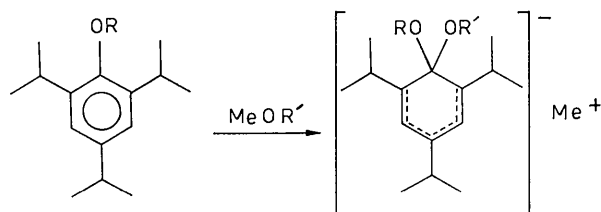*Istituto di Chimica Fisica, Università di Milano, Milano, Italy*

The crystal structures of two so-called Meisenheimer salts, the complexes of 2,4,6-trinitrophenetole with caesium or potassium ethoxide, have been determined and refined by three-dimensional least-squares methods. The caesium salt is monoclinic, space group $P2_1/c$, with $a=15\cdot564$, $b=10\cdot54$, $c=19\cdot919$ Å, $\beta=110\cdot31°$ and eight molecules per unit cell, whereas the potassium salt is triclinic, space group $P\bar{1}$, with $a=14\cdot744$, $b=10\cdot285$, $c=9\cdot992$ Å, $\alpha=105\cdot9°$, $\beta=104\cdot0°$, $\gamma=97\cdot2°$ and four molecules per unit cell. Although true isomorphism cannot be claimed, there is a definite geometrical analogy between the two structures. Intensity data were collected visually from Weissenberg photographs. The final R index is $0\cdot102$ for the caesium salt and $0\cdot064$ for the potassium salt. In the latter, the average standard deviations for bond lengths and angles are $0\cdot008$ Å and $0\cdot6°$; these data are given uncorrected for thermal motion.

In both compounds two equivalent alkoxyl groups are attached to the same carbon atom, which attains tetrahedral (sp^3) configuration; this is in agreement with theoretical predictions and spectroscopic or kinetic data. The six-membered ring derived from the parent aromatic compound is still virtually planar; deformation from a regular hexagon, which is required by the presence of one tetrahedral carbon atom, is evidenced in variations of the C–C bond lengths. For the potassium salt, a case of structural disorder is observed relative to one ethoxyl group; both theoretical and experimental evidence for this situation are given.

Introduction

In recent years, the structures of possible intermediates or activated complexes in aromatic substitution reactions have been the object of considerable interest (Bunnett, 1959; Ross, 1963; Simonetta & Carrà, 1964; Carrà, Raimondi & Simonetta, 1966). In a few examples of nucleophilic substitution reactions a stable intermediate has been isolated; the complexes of alkyl picrates with alkali alkoxides ('Meisenheimer salts'), which are relatively easy to obtain in good crystals, have been well known for a long time (Meisenheimer, 1902):

Among these compounds, the complexes of ethyl picrate (2,4,6-trinitrophenetole) with alkali ethoxides appeared to be the most suitable for crystallographic use, because of their stability and the absence of 'crys-

tallization' alcohol or water. The determination of the unit cell showed these structures to be rather complex, owing to the presence of two independent molecules in the asymmetric unit (Destro, Gramaccioli, Mugnoli & Simonetta, 1965). For this reason, a derivative containing a particularly heavy atom, such as Cs, was considered at the beginning; then, after solution of the structure, in order to get better experimental evidence on the molecular geometry, our attention was turned to the corresponding potassium salt, whose unit cell had shown definite structural relations to the caesium compound. Preliminary announcements of our results have already been given (Casalone, Destro, Gramaccioli, Mariani, Mugnoli & Simonetta, 1966; Destro, Gramaccioli & Simonetta, 1967).

Experimental

Crystals of the two complex salts were obtained from reaction of 2,4,6-trinitrophenetole with the corresponding alkali ethoxide and recrystallization of the product from ethanol. They are bright red, acicular, elongated along **b**. The unit-cell dimensions for the two compounds are given in Table 1.* For the potassium salt, these were obtained from a least-squares treatment of 131 measurements on zero-level Weissenberg photographs taken at 20 °C about the three crystallographic axes; for the Cs salt, the same treatment was applied to 28 reflexions on a zero-level Weissenberg photograph taken at the same temperature around the *b* axis, with Cu $K\alpha$ radiation (λ Cu $K\alpha_1 = 1.54051$ Å, λ Cu $K\alpha_2 = 1.54433$ Å).

In these measurements the film was held in the asymmetric position, essentially following the technique of Straumanis. Eccentricity coefficients were included as parameters in the least-squares calculations and weights were assigned as inversely proportional to $\sin^2 2\theta$. The value of *b* was obtained from a least-squares treatment of 9 measurements on the zero level of the axis [111]. In this case the film was held in the symmetric position, the apparent radius of the camera being obtained by internal calibration, using the $h0\bar{h}$ reflexions.

The densities of the two substances, reported in Table 1, were measured by flotation and lead to $Z=8$ for the Cs salt and $Z=4$ for the K salt; from these experimental data some geometrical analogy between the unit cells of the Meisenheimer salts here examined is evident, although no true isomorphism can be claimed.

For the caesium salt, all reflexions of the type $h0l$ with *l* odd were absent. Because of the scarcity of data taken about axes other than **b**, at the beginning no reliable conclusion could be drawn about the extinc-

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* In Table 1, the standard deviations of the cell parameters were derived from the residuals and the diagonal elements of the inverse matrix in the least squares; their particularly low values do not seem to be very significant, apart from confirming the internal consistency of the data here used.

Table 1. *Unit cell data* (*at* 20 °C)

	Caesium 'Meisenheimer' complex $CsC_{10}H_{12}N_3O_8$	Potassium 'Meisenheimer' complex $KC_{10}H_{12}N_3O_8$
a	15.564 ± 0.003 Å	14.7443 ± 0.0008 Å
b	10.54 ± 0.02 Å	10.2848 ± 0.0004 Å
c	19.919 ± 0.001 Å	9.9919 ± 0.0004 Å
α	–	$105.901° \pm 0.006°$
β	$110.31° \pm 0.01°$	$104.05° \pm 0.01°$
γ	–	$97.15° \pm 0.01°$
System	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Z	8	4
Cell volume	3064.4 Å^3	1383.6 Å^3
D_{calc}	1.890 g.cm^{-3}	1.638 g.cm^{-3}
D_{meas}	1.878 g.cm^{-3}	1.640 g.cm^{-3}

tions along $0k0$; the space group $P2_1/c$ was therefore confirmed only after solution of the structure.

For the potassium salt, the absence of piezoelectricity seemed to indicate the space group $P\bar{1}$; this choice was fully confirmed by solution of the structure.

Intensity data were collected from multiple-film equi-inclination Weissenberg photographs. For the caesium salt, the layers 0–4 and 5–7 around **b** were obtained from two needle-shaped crystals, almost square in section, whose diameters were respectively about 0·1 and 0·08 mm. The layers 0 and 1 around [111] were obtained from an irregularly shaped crystal, whose diameter was approximately 0·24 mm. For the potassium salt, the layers 0 to 8 along **a**, 0 to 3 along **c** and the 0 layer along **b** were collected from three different needle-shaped crystals, almost square in section, whose diameters were about 0·1 mm. Copper $K\alpha$ radiation was always used and the intensities were estimated visually and corrected for Lorentz and polarization factors. For the potassium salt, no corrections either for absorption or extinction were made, whereas for the caesium salt absorption was approximatively accounted for, assuming the prismatic crystals to be cylindrical and the irregularly shaped crystal to be spherical.

The processing of the observed data was first carried on within the single layers, using a method rather similar to the procedure mentioned by Rae (1965). The second stage, which involved the evaluation of relative scale factors for all the layers and subsequent averagings of the observed $|F|^2$, was performed according to the method proposed by Rollett & Sparks, modified in order to account for the dependence of weights upon the final scale factors (Hamilton, Rollett & Sparks, 1965; Duchamp, 1964). The assignment of estimated standard deviations to the individual observations, which is the major difference between Rae's method and ours, will be described elsewhere (Gramaccioli & Mariani, 1967). Of 6988 and 6356 independent reflexions within the effective spheres of Cu $K\alpha$ radiation for the caesium and the potassium salts, respectively, 4005 and 4137 were collected, of which 1456 and 1275 were too weak to be observed.

Determination and refinement of the structures

For the caesium salt, a sharpened three-dimensional Patterson synthesis gave the positions of the heavy atoms. A three-dimensional Fourier synthesis revealed the positions of all the remaining atoms, except hydrogen. For the potassium salt, in view of the similarity between the unit cells of these two compounds, it was considered probable that a structural analogy might be particularly evident on the (010) projections, because of the equal lengths of the b axes and the coincidence of screw axes with centres of symmetry.

From the Patterson syntheses calculated on these projections, a close similarity between the two substances was soon confirmed, provided the a axis of the potassium derivative was brought to coincidence with the [201] direction in the Cs compound, as shown in Fig. 1. On this basis, the coordinates x and z were assigned to each atom in the new structure, except hydrogen atoms. With these parameters, a first structure factor calculation for the potassium salt in the (010) projection gave an R index of 0·41.

The assignment of the y coordinates was less simple. After some unsuccessful attempts, based on geometrical considerations, phasing was tried with the help of the potassium atoms, whose positions were derived from a three-dimensional Patterson synthesis. This synthesis served also as a check of the situation as found on the (010) projection. Although the corresponding R index was about 0·65, structure factors on the (001) and (100) projections gave a Fourier synthesis with enough information to be interpreted, with the help of the assumed x and z coordinates.
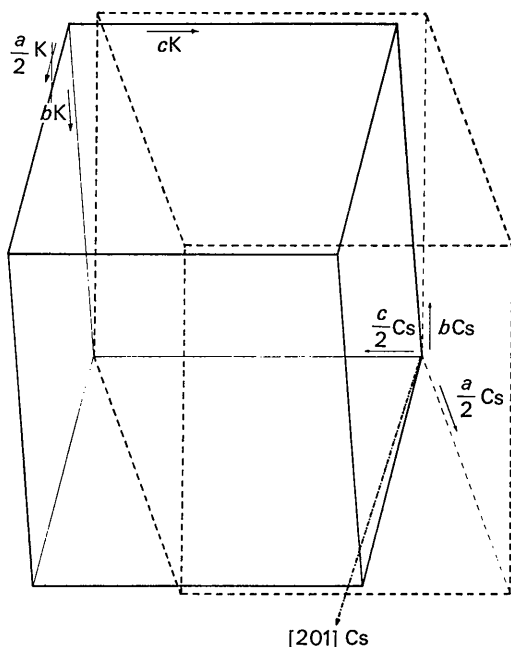
Refinement of the two structures was first carried on by difference Fourier synthesis, until the R indices for the three-dimensional data were equal to 0·15 and 0·18 for the caesium and the potassium salts respectively. Further refinement by block-diagonal least squares was then tried, minimizing the function

$$\Sigma \, w(|F|_{\mathrm{obs}} - |F|_{\mathrm{calc}})^2.$$

Weights were assigned according to the function

$$w = 1/(a + |F|_{\mathrm{obs}} + c|F|_{\mathrm{obs}}^2) \, ,$$

where a and c were chosen so as to lead to an approximately constant value of $w(|F|_{\mathrm{obs}} - |F|_{\mathrm{calc}})^2$ as a function of $|F|_{\mathrm{obs}}$. The reflexions too weak to be measured ('less than') were not included in the least squares. For the caesium salt, the reflexions with an observed structure factor greater than 120 were also omitted. All temperature factors were considered as isotropic and hydrogen atoms were omitted from the structure factor calculations. Convergence was soon attained at an R index of about 0·14 for both structures.

After this stage of the refinement, however, the geometry of one of the ethoxyl groups in the potassium salt was rather questionable, the length of the 'paraffinic' C(7')–C(8') bond being only 1·27 Å. Introducing anisotropic temperature factors did not improve the situation. At the position of the atoms C(7') and C(8') on a three-dimensional difference Fourier synthesis, a large positive region appeared instead of definite peaks. In this region, it was impossible to locate the two carbon atoms without arriving at a geometrical situation inadmissible for an ethoxyl group.

A reasonable interpretation of the difference map was made on the basis of disorder in the structure, the proposed model consisting of a statistical distribution of two carbon atoms in two principal positions, in equal amounts. This model accounted for the absence of definite peaks in the map and permitted a more reasonable set of distances and angles in the ethoxyl group (C–C bonds about 1·40 Å; C–O bonds 1·47 and 1·43 Å; C–O–C angles 117° and 111° and O–C–C angles 115° and 112°). One least-squares refinement cycle, starting with these new coordinates, led to only small changes in the R index and the molecular geometry. At this stage, we looked for further evidence and a possible theoretical explanation for the partial disorder in the structure, by carrying out systematic calculations of the repulsion energy between the atoms in the ethoxyl group and the adjacent atoms in the crystal as a function of the angles of rotation φ_1 and φ_2 around the bonds O(7')–C(7') and C(1')–O(7'). In these calculations, the total repulsion energy was obtained by summing the contributions of all the pairs of non-bonded atoms whose distance r was less than the 'touching distance' r_0, i.e. the sum of their van der Waals radii [1·33 Å for K$^+$, 1·6 Å for C, 1·5 Å for N, 1·4 Å for O, and 2·0 Å for methylene and methyl groups, in essential agreement with Pauling (1960)].

Fig. 1. Geometrical relationships between the unit cells of the two compounds.

Table 2. *Observed and calculated structure factors for the potassium salt*

The columns contain values of h, k, F_{obs}, F_{calc}. Reflexions marked with an asterisk were given zero weight in the least-squares refinement. 'Less than' reflexions are indicated with a negative observed structure factor.

Table 2 (*cont.*)

The repulsion energy between each pair of atoms was evaluated according to the expression:

$$E = -0.14(r/r_0)^6 + 3.10^4 \exp(-13\,r/r_0) \text{ kcal. mole}^{-1} \quad (1).$$

This formula is similar to a function proposed by Kitaigorodskii (1961), in which the constants have been modified on the basis of previous experience in anal-

ogous calculations, where particularly good results were obtained (Casalone, Mariani, Mugnoli & Simonetta, 1967). The different models at the starting point ($\varphi_1 = 0°$; $\varphi_2 = 0°$) had essentially the geometry resulting from the last cycle of least squares, with the exception that atoms C(7') and C(8') were placed in the plane of O(7'), C(1') and O(8'), with the O(7')–C(7') bond

Table 3. *Observed and calculated structure factors for the caesium salt*

The columns contain values of h, k, F_{obs}, F_{calc}. Reflexions marked with an asterisk were given zero weight in the least-squares refinement. 'Less than' reflexions are indicated with a negative observed structure factor.

L = 0			
1	0	1348*	1697
1	1	979*	-1238
1	2	315	397
1	3	486	507
1	4	935	-960
1	5	935	701
1	6	496	-411
1	7	949*	-890
2	0	1630*	-1866
2	1	607	-583
2	2	832	744
2	3	1013	966
2	4	1764*	1992
2	5	714	962
2	6	543	-422
2	7	909	-773
3	0	1757*	-2127
3	1	1351*	1428
3	2	168	-143
3	3	989	958
3	4	845	712
3	5	674	-794
3	6	205	262
3	7	-184	29
4	0	2434*	-2618
4	1	754	751
4	2	929	-890
4	3	144	-212
4	4	919	925
4	5	1153*	-1287
4	6	1174*	1104
4	7	647	616
5	0	1086	-1158
5	1	1801*	-1965
5	2	396	-318
5	3	1566*	-1706
5	4	614	-610
5	5	852	918
5	6	952*	983
5	7	610	524
6	0	419	-335
6	1	1143*	-1248
6	2	184	143
6	3	1143*	-1239
6	4	550	-605
6	5	795	891
6	6	570	-584
6	7	335	281
7	0	604	613
7	1	-121	01
7	2	691	736
7	3	315	274
7	4	-194	-58
7	5	-151	-176
7	6	778*	-1218
7	7	-198	-20
7	8	-248	115
8	0	342	386
8	1	1465*	1508
8	2	-158	101
8	3	999	1004
8	4	506	-525
8	5	718	-752
8	6	329	-361
8	7	268	-221
9	0	912*	1120
9	1	791	806
9	2	436	-351
9	3	969	1033
9	4	308	-320
9	5	-174	-209
9	6	557	569
9	7	503	-522
10	0	208	-291
10	1	228	-226
10	2	255	-291
10	3	345	272
10	4	312	240
10	5	503	501
10	6	369	334
10	7	402	-395
11	0	1106*	-1270
11	1	315	-346
11	2	-188	-19
11	3	-255	-159
11	4	919	897
11	5	188	-81
11	6	-191	53
11	7	-345	64
12	0	513	-569
12	1	-164	117
12	2	-194	03
12	3	453	-434
12	4	-248	202
12	5	208	-168
12	6	-188	-12
12	7	379	374
13	0	701	699
13	1	-168	-38
13	2	-194	40
13	3	369	-315
13	4	449	-469
13	5	-181	-221
13	6	235	-83
13	7	285	297
14	0	775	743
14	1	201	-144
14	2	-191	35
14	3	-251	-126
14	4	483	-518
14	5	-168	144
14	6	-161	-71
14	7	-268	5
15	0	184	177
15	1	-154	-109
15	2	-178	96
15	4	-211	-148
15	7	-221	-163
16	0	215	-220
16	1	198	224
17	0	218	-185
17	1	168	183
18	0	54	-73
18	1	-91	-10
L = 1			
0	1	835	796
0	2	262	493
0	3	624	670
0	4	362	-390
0	5	989	-888
0	6	-54	-28
-1	1	456	459
-1	2	1854*	-3182
1	3	593	577
-1	3	902*	1006
1	4	409	-294
-1	4	198	237
1	5	654	-534
-1	5	604	-545
1	6	768	-797
-1	6	1210*	1137
1	7	-174	-229
-1	7	748	-885
2	1	262	243
-2	1	1244*	1557
2	2	372	-125
-2	2	2558*	-2645
2	3	1234*	-1195
-2	3	704	-690
2	4	1381*	1646
-2	4	198	-197
2	5	-104	61
-2	5	694	697
2	6	436	-316
-2	6	902	794
2	7	593	581
-2	7	590	465
3	1	1355*	-1492
3	2	1516*	-1510
-3	2	687	669
3	3	-131	-75
-3	3	1127*	-1110
3	4	868	908
-3	4	1039	-1126
3	5	815	959
-3	5	1053	1283
3	6	201	207
-3	6	134	122
3	7	372	468
-3	7	842	856
4	1	2545*	-2933
-4	1	946	-987
4	2	1117*	-1026
-4	2	1717*	1648
4	3	1807*	2125
-4	3	1133*	1134
4	4	-151	100
-4	4	141	-31
4	5	751	785
-4	5	996*	1132
4	6	329	332
-4	6	567	-118
4	7	583	-517
-4	7	-208	-7
5	1	855	-880
-5	1	972	-753
5	2	449	-429
-5	2	969	750
5	3	684	693
-5	3	899	876
5	4	1190*	-1347
-5	4	295	226
5	5	184	134
-5	5	-124	140
5	6	-144	64
-5	6	376	-353
5	7	-235	-119
-5	7	590	-510
6	1	1291*	1354
-6	1	845	876
6	2	503	456
-6	2	-127	-85
6	3	1452*	-1626
-6	3	-178	15
6	4	956	-965
-6	4	1127*	1213
6	5	278	-349
-6	5	778	-813
6	6	-158	-66
-6	6	181	-160
6	7	382	396
-6	7	-255	-39
6	8	768	768
7	1	1482*	1549
-7	1	1100	1106
7	2	567	-482
-7	2	459	474
7	3	1086	-1159
-7	3	1167*	-1196
7	4	463	442
-7	4	-191	100
7	5	684	-756
-7	5	614	-851
7	6	-168	162
-7	6	-161	-104
7	7	282	211
-7	7	282	227
8	1	436	354
-8	1	158*	29
8	2	198	-274
-8	2	308	323
8	3	-221	207
-8	3	211	-243
8	4	845	860
-8	4	922	-939
8	5	563	-581
-8	5	459	-429
8	6	-178	121
-8	6	-174	-81
8	7	295	-308
-8	7	-290	28
8	8	426	-700
-8	8	677	704
9	1	386	-467
-9	1	835	-849
9	2	1207*	1079
-9	2	503	-439
9	3	751	744
-9	3	758	727
9	4	325	312
-9	4	667	-617
9	5	-178	-144
-9	5	-171	119
9	6	312	-293
-9	6	-184	139
9	7	386	-357
-9	7	315	-318
-9	8	681	683
10	1	614	-654
-10	1	1049	-1065
10	2	976	935
-10	2	956	-915
10	3	-248	34
-10	3	748	734
10	4	-241	-207
-10	4	-235	144
10	5	490	573
-10	5	362	379
10	6	285	-316
-10	6	251	280
10	7	-305	131
-10	7	329	-144
11	1	228	-177
-11	1	248	-243
11	2	191	-190
-11	2	228	-242
11	3	-258	-182
-11	3	312	-319
11	4	-248	-60
-11	4	583	527
11	5	339	385
-11	5	593	626
-11	6	-191	113
11	7	372	329
-11	7	-359	276
12	1	-168	33
-12	1	164	161
12	2	1029	-989
-12	2	818	704
12	3	-262	-195
-12	3	262	-334
12	4	-248	-158
-12	4	-248	14
-12	5	-184	52
12	5	188	149
12	6	325	364
-12	6	251	-243
12	7	-302	84
-12	7	335	217
13	1	-168	-29
-13	1	168	163
13	2	821	-663
-13	2	610	615
13	3	258	263
-13	3	-262	117
13	4	-241	-161
-13	4	-245	64
13	5	198	-140
-13	5	-181	-175
13	6	228	263
-13	6	181	-217
13	7	-275	-170
-13	7	-312	-148
14	1	198	164
-14	1	235	191
14	2	-188	158
-14	2	-191	-84
14	3	248	80
-14	3	-255	148
14	4	-225	-141
-14	4	-235	-54
14	5	231	-249
-14	5	275	-352
14	6	191	-47
-14	6	-168	18
14	7	-238	-188
-14	7	-312	-210
15	1	342	358
-15	1	158	196
15	2	449	407
-15	2	503	-514
15	4	-201	22
-15	4	-215	24
16	1	-134	65
-16	1	161	47
17	1	194	-178
-17	1	151	-137
18	1	168	-197
-18	1	205	-196
-19	1	-54	-76
L = 2			
0	0	1546*	2016
0	3	543	553
0	4	1945*	-3102
0	5	624	596
0	6	-77	-50
0	7	201	-297
1	0	87	-77
-1	0	2159*	2561
1	1	231	-266
-1	1	1103*	-1310
1	2	577	542
-1	3	986	-981
1	4	285	-293
-1	4	1247*	-1397
1	5	583	616
-1	5	889	-896
1	6	880	-1093
-1	6	536	500
1	7	697	-796
-1	7	878	801
2	0	493	621
-2	0	3226*	-3476
2	1	952	957
-2	1	466	478
2	2	241	239
-2	2	-74	-158
2	3	1495*	1598
-2	3	1170*	-1581
2	4	453	420
-2	4	1479*	1596
2	5	329	243
-2	5	1039	-1073
2	6	687	-745
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12	2	-174	-90
-12	2	-191	-36
12	3	-225	-208
-12	3	550	453
-12	4	-248	-153
-12	5	248	-263
-12	6	-191	216
-12	7	-342	-175
13	0	131	-107
-13	0	332	341
13	1	349	-336
-13	1	268	338
13	2	-154	81
-13	2	194	215
13	3	-198	-310
-13	3	-262	68
13	4	-171	64
-13	4	-248	-237
-13	5	228	-173
-13	6	-228	-244
-13	7	-322	44
14	0	104	47
-14	0	191	206
14	1	-114	29
-14	1	221	-185
14	2	-127	131
-14	2	275	337
14	3	-161	-79
-14	3	258	-301
-14	4	-241	-11
-14	6	376	-410
15	0	221	231
-15	0	218	225
15	1	151	160
-15	1	352	-365
15	2	-94	41
-15	2	-191	-9
-15	4	-228	-247
-16	0	117	79
-16	1	205	-153
-17	0	221	-258
-17	1	-141	83
-18	0	208	-193
-18	1	-121	134
-19	0	-57	-46
-19	1	-97	-12
-20	0	-30	185
-20	1	-50	35
L = 9			
0	1	1448*	1662
0	2	751	-781
0	-3	1435*	-1397
0	4	-194	-77
0	5	295	-260
0	6	201	199
0	7	322	310
0	9	292	79
0	10	-184	73
1	1	624	708
-1	1	701	745
1	2	573	-558
-1	2	523	-541
1	3	436	334
-1	3	805	-757
1	4	721	778
-1	4	1153*	-1246
1	5	600	-690
-1	5	181	192
1	6	-171	126
-1	6	215	226
1	7	483	-501
-1	7	389	426
-1	8	701	800
2	1	-131	-82
-2	1	805	-881
2	2	734	626
-2	2	463	-474
2	3	701	673
-2	3	1308*	1242
2	4	412	400
-2	4	885*	-1035
2	5	319	-351
-2	5	473	463
2	6	412	-364
-2	6	-161	139
2	7	536	-462
-2	7	292	-313
-2	8	614	716
3	1	640	-660
-3	1	1120*	-1365
3	2	1988*	1991
-3	2	476	496
3	3	-225	145
-3	3	1502*	1400
3	4	288	-257
-3	4	386	385
3	5	453	477
-3	5	637	622
3	6	570	-614
-3	6	-161	8
3	7	-298	100
-3	7	369	-323
4	1	349	-353
-4	1	526	-620
4	2	473	432
-4	2	292	-274
4	3	637	-576
-4	3	-194	-62
4	4	228	217
-4	4	1006*	1085
4	5	687	765
-4	5	412	455
4	6	-188	-75
-4	6	-161	145
4	7	557	561
-4	7	282	200
5	1	215	-269
-5	1	976*	1114
5	2	1646*	-1606
-5	2	510	500
5	3	-245	-162
-5	3	999	-939
5	4	312	283
-5	4	469	438
5	5	288	304
-5	5	205	-253
5	6	540	591
-5	6	235	-221
5	7	305	295
-5	7	503	428
6	1	426	-442
-6	1	268	219
6	2	1288*	-1193
-6	2	1485*	1765
6	3	664	636

Table 3 (cont.)

length equal to 1·43 Å and the C(7′)–C(8′) bond lengths equal to 1·50, 1·53, 1·54 or 1·55 Å, respectively. The C(1′)–O(7′)–C(7′) and the O(7′)–C(7′)–C(8′) angles were assumed to be equal to 110° or 115°; a different series of calculations was performed for every possible combination of these bond lengths and angles. For each model, φ_1 and φ_2 were varied in the range $-90°$ to $+140°$ and $-50°$ to $+50°$ respectively; the scanning interval for the rotations was 10°.

These operations ended in showing the existence of two definite points of minimum for repulsion energy, almost equivalent (within 0·2 kcal.mole⁻¹) and virtually independent of the starting model. The rotation angles φ_1 and φ_2 were equal to $-50°$ and $-10°$ in one case and $+90°$ and $+20°$ in the other, in good agreement with the experimental values of $\varphi_1 = -51°$, $\varphi_2 = -15°$

and $\varphi_1 = +110°$, $\varphi_2 = +20°$ derived from the difference map.

For the caesium salt (radius of $Cs^+ = 1·67$ Å), a similar series of calculations for the corresponding ethoxyl group indicated the presence of two points of minimum for all the models, as in the case of the potassium salt, but with a greater difference in energy (0·5 to 1·0 kcal.mole⁻¹). This could explain the virtual absence of disorder in the structure; the minimum corresponding to the lower energy was situated at $\varphi_1 = -60°$ and $\varphi_2 = 0°$, in good agreement with the experimental results.

At this stage, refinement of both structures was continued by block-diagonal least squares, using a program written for the IBM 7040 computer by Albano, Domenicano & Vaciago (1966). In the potassium salt,

Table 4. *The heavy-atom parameters and their standard deviations in the potassium salt*

All the values in the table have been multiplied by 10⁴. The temperature factor is in the form
$$T_i = \exp\left[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)\right].$$

	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
K(1)	7838 (1)	2704 (1)	9108 (1)	44 (1)	28 (1)	50 (1)	70 (1)	59 (1)	77 (1)
K(2)	1377 (1)	1653 (1)	1514 (1)	32 (1)	18 (1)	43 (1)	76 (1)	71 (2)	107 (1)
C(1)	8609 (4)	2674 (4)	6121 (5)	27 (2)	28 (5)	38 (6)	75 (4)	51 (6)	62 (4)
C(2)	8764 (4)	3615 (4)	5230 (5)	31 (3)	30 (6)	29 (7)	65 (4)	35 (7)	87 (5)
C(3)	8955 (4)	3222 (5)	3936 (5)	32 (3)	19 (6)	36 (7)	95 (4)	67 (7)	65 (4)
C(4)	9061 (4)	1866 (5)	3336 (5)	35 (3)	26 (6)	39 (7)	91 (4)	48 (7)	66 (5)
C(5)	8991 (4)	912 (5)	4099 (5)	30 (3)	36 (6)	34 (7)	84 (4)	43 (8)	87 (5)
C(6)	8783 (4)	1276 (5)	5374 (5)	38 (3)	38 (6)	49 (7)	71 (4)	66 (7)	94 (5)
C(7)	6908 (4)	2113 (7)	5038 (6)	31 (3)	27 (9)	12 (8)	178 (8)	73 (11)	87 (6)
C(8)	6058 (6)	1476 (10)	5278 (8)	52 (4)	−63 (13)	9 (11)	296 (13)	128 (16)	123 (8)
C(9)	10212 (5)	3449 (9)	7759 (7)	32 (3)	17 (11)	26 (9)	260 (11)	95 (14)	104 (7)
C(10)	10731 (6)	3713 (11)	9226 (10)	43 (4)	48 (13)	−33 (14)	299 (14)	112 (20)	183 (12)
C(1′)	3660 (4)	2693 (4)	1428 (5)	34 (3)	30 (5)	26 (7)	65 (4)	41 (6)	60 (4)
C(2′)	4242 (4)	1582 (4)	1466 (5)	41 (3)	26 (6)	43 (7)	54 (3)	47 (6)	83 (5)
C(3′)	5169 (4)	1689 (5)	1487 (5)	36 (3)	37 (6)	41 (7)	81 (4)	49 (7)	68 (5)
C(4′)	5686 (4)	2945 (5)	1513 (5)	24 (2)	29 (6)	38 (7)	83 (4)	45 (7)	75 (5)
C(5′)	5229 (4)	4072 (5)	1490 (5)	42 (3)	24 (6)	57 (7)	69 (4)	36 (7)	79 (5)
C(6′)	4316 (4)	3970 (4)	1480 (5)	30 (3)	24 (5)	46 (7)	65 (4)	51 (7)	92 (5)
C(7a′)	2901 (10)	2276 (11)	−1226 (13)	69 (8)	23 (16)	24 (20)	66 (10)	−47 (20)	90 (13)
C(7b′)	3013 (11)	1531 (13)	−1166 (13)	107 (9)	189 (15)	44 (20)	157 (13)	6 (22)	64 (13)
C(8a′)	3377 (12)	1361 (18)	−1925 (15)	75 (9)	133 (24)	82 (21)	266 (24)	−48 (35)	80 (16)
C(8b′)	2626 (17)	2203 (14)	−2249 (15)	192 (20)	50 (27)	76 (30)	114 (12)	122 (20)	136 (15)
C(9′)	3889 (5)	3505 (8)	4013 (7)	46 (4)	21 (10)	34 (10)	182 (9)	6 (14)	88 (7)
C(10′)	3474 (7)	3133 (12)	5063 (8)	87 (7)	−62 (18)	47 (12)	386 (18)	128 (18)	100 (8)
N(1)	8676 (4)	5038 (4)	5798 (5)	51 (3)	33 (5)	45 (7)	68 (3)	73 (7)	136 (6)
N(2)	9260 (4)	1469 (5)	2013 (5)	36 (3)	17 (7)	34 (6)	146 (5)	68 (8)	85 (5)
N(3)	8717 (3)	228 (4)	6090 (5)	37 (2)	34 (5)	46 (7)	95 (4)	125 (6)	137 (5)
N(1′)	3763 (3)	276 (4)	1483 (5)	51 (3)	28 (5)	72 (7)	70 (3)	60 (7)	113 (5)
N(2′)	6631 (3)	3059 (5)	1484 (5)	34 (2)	38 (6)	42 (6)	110 (4)	49 (7)	88 (5)
N(3′)	3911 (4)	5184 (4)	1496 (5)	51 (3)	34 (5)	61 (7)	75 (3)	68 (6)	105 (5)
O(1)	8500 (4)	5422 (4)	6950 (5)	103 (3)	72 (6)	104 (8)	92 (4)	23 (8)	152 (6)
O(2)	8836 (4)	5837 (4)	5127 (5)	101 (3)	81 (6)	164 (8)	103 (3)	203 (7)	262 (6)
O(3)	9352 (3)	2342 (5)	1363 (4)	57 (3)	52 (6)	81 (6)	193 (5)	146 (6)	101 (4)
O(4)	9372 (3)	276 (5)	1492 (5)	71 (3)	73 (6)	77 (7)	150 (5)	1 (9)	113 (5)
O(5)	8850 (3)	−917 (3)	5524 (5)	84 (3)	62 (5)	100 (7)	74 (3)	111 (6)	187 (5)
O(6)	8520 (3)	509 (4)	7241 (4)	85 (3)	88 (6)	145 (6)	144 (4)	208 (6)	168 (4)
O(7)	7690 (2)	2560 (3)	6316 (3)	25 (1)	23 (4)	28 (4)	105 (3)	56 (5)	71 (3)
O(8)	9201 (3)	3234 (3)	7587 (3)	32 (2)	16 (4)	25 (5)	94 (3)	43 (5)	70 (3)
O(1′)	2900 (3)	76 (4)	1355 (5)	58 (2)	15 (5)	137 (6)	75 (3)	67 (7)	212 (6)
O(2′)	4215 (3)	−629 (3)	1626 (4)	73 (3)	43 (5)	60 (7)	80 (3)	120 (6)	166 (5)
O(3′)	7018 (3)	2037 (4)	1442 (5)	40 (2)	59 (5)	59 (6)	140 (4)	95 (7)	142 (5)
O(4′)	7079 (3)	4141 (4)	1452 (5)	39 (2)	5 (5)	73 (6)	126 (4)	109 (7)	180 (6)
O(5′)	4435 (4)	6263 (4)	1595 (5)	82 (3)	51 (5)	100 (7)	72 (3)	117 (6)	201 (6)
O(6′)	3066 (3)	5118 (4)	1438 (5)	55 (2)	90 (5)	113 (6)	116 (3)	151 (7)	203 (6)
O(7′)	2830 (3)	2262 (3)	220 (4)	33 (2)	19 (4)	30 (5)	95 (3)	27 (6)	78 (4)
O(8′)	3241 (3)	2940 (3)	2585 (3)	33 (2)	18 (4)	44 (5)	87 (3)	25 (5)	68 (3)

anisotropic temperature factors were assigned to all the atoms except hydrogen; for the caesium salt, anisotropic temperature factors were assigned only to the two heavy metal atoms. Weights were taken as before, but with a and c taken as the minimum observed $|F|$ and the reciprocal of the maximum observed structure factor, respectively, in substantial agreement with the weighting scheme proposed by Cruickshank et al. (1961). Hydrogen atoms were not considered in the case of the caesium salt; for the potassium compound, the hydrogen atoms of the rings and of the three ordered CH_2 groups were introduced in the structure factor calculations, with positional coordinates derived from the presumed geometry of the molecule (C–H bond lengths = 1·00 Å; C–C–H bond angles = 109·5° or 120°) and temperature factors $B = 4$ Å². Some of the

strongest reflexions (77 for the K salt and 275 for the Cs salt) were not included in these cycles of least squares, because they were suspected to suffer from extinction or related factors; their number is much higher for the caesium compound, where all observations with $|F|_{obs}$ greater than 110 were systematically omitted. After three cycles of least squares ($R = 0·075$), a three-dimensional difference Fourier synthesis was calculated for the potassium salt, in order to locate the remaining hydrogen atoms; except for the 'disordered' ethoxyl group, clear peaks (0·25 eÅ⁻³) appeared for all of them, and they were introduced into the next structure factor calculations with a thermal factor $B = 4·5$ Å². At the end of the refinement, no shift exceeded one-half of the standard deviation of the corresponding parameter, except for B_{11} of Cs(1), where the final shift

Table 5. *Atomic parameters and their standard deviations in the caesium salt*

The anisotropic temperature factor coefficients (only for Cs atoms) have been multiplied by 10^4; for these, the expression for T_i is the same as in Table 4. Standard deviations, as here reported, are on the same scale as the last digit of the corresponding parameters. Isotropic temperature factor coefficients are given in Å².

	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Cs(1)	0·2200 (1)	0·3453 (2)	0·0652 (1)	66 (1)	−8 (2)	15 (1)	100 (2)	6 (1)	27 (0)
Cs(2)	0·8582 (1)	0·0998 (2)	0·0105 (1)	50 (1)	2 (2)	13 (1)	104 (2)	−8 (1)	35 (0)
C(1)	0·1377 (14)	0·1108 (25)	0·3660 (11)			$B = 5·6$ (5)			
C(2)	0·1293 (15)	0·2207 (27)	0·3167 (12)			6·0 (5)			
C(3)	0·1081 (12)	0·2221 (24)	0·2445 (10)			4·5 (4)			
C(4)	0·0940 (12)	0·1042 (22)	0·2135 (9)			4·2 (4)			
C(5)	0·0938 (14)	−0·0127 (26)	0·2516 (11)			5·7 (5)			
C(6)	0·1169 (12)	−0·0085 (22)	0·3215 (10)			4·5 (4)			
C(7)	0·3013 (13)	0·0961 (25)	0·3951 (11)			5·3 (5)			
C(8)	0·3857 (22)	0·0872 (38)	0·4542 (18)			9·8 (9)			
C(9)	−0·0117 (14)	0·1308 (24)	0·3707 (11)			5·3 (5)			
C(10)	−0·0623 (24)	0·1351 (40)	0·4212 (19)			10·3 (10)			
C(1')	0·6188 (12)	0·3560 (22)	0·3873 (10)			4·4 (4)			
C(2')	0·5545 (13)	0·4668 (26)	0·3609 (10)			5·3 (4)			
C(3')	0·4635 (13)	0·4591 (25)	0·3172 (10)			5·0 (4)			
C(4')	0·4244 (12)	0·3402 (22)	0·2956 (9)			4·2 (4)			
C(5')	0·4759 (12)	0·2259 (24)	0·3147 (10)			4·7 (4)			
C(6')	0·5611 (14)	0·2345 (26)	0·3564 (11)			5·7 (5)			
C(7')	0·6809 (21)	0·3784 (33)	0·2902 (16)			8·9 (8)			
C(8')	0·7307 (21)	0·2934 (40)	0·2663 (17)			9·7 (9)			
C(9')	0·5952 (16)	0·3479 (26)	0·5000 (12)			6·3 (5)			
C(10')	0·6508 (24)	0·3509 (36)	0·5789 (18)			9·6 (9)			
N(1)	0·1442 (15)	0·3518 (25)	0·3548 (12)			8·1 (6)			
N(2)	0·0724 (11)	0·0965 (20)	0·1365 (9)			5·6 (4)			
N(3)	0·1214 (12)	−0·1273 (21)	0·3595 (10)			6·3 (4)			
N(1')	0·5919 (15)	0·5925 (26)	0·3848 (12)			8·2 (6)			
N(2')	0·3318 (12)	0·3343 (19)	0·2442 (9)			5·6 (4)			
N(3')	0·6164 (14)	0·1147 (23)	0·3798 (11)			7·1 (5)			
O(1)	0·1749 (15)	0·3546 (23)	0·4190 (11)			9·8 (6)			
O(2)	0·1196 (15)	0·4423 (28)	0·3137 (12)			10·8 (6)			
O(3)	0·0694 (11)	0·1943 (20)	0·1037 (9)			7·5 (4)			
O(4)	0·0599 (12)	−0·0102 (20)	0·1086 (9)			8·0 (4)			
O(5)	0·1011 (12)	−0·2265 (22)	0·3220 (10)			8·8 (5)			
O(6)	0·1370 (13)	−0·1249 (21)	0·4227 (11)			8·6 (5)			
O(7)	0·2272 (8)	0·1041 (15)	0·4197 (7)			4·8 (3)			
O(8)	0·0841 (9)	0·1240 (16)	0·4090 (7)			5·4 (3)			
O(1')	0·6742 (15)	0·5968 (24)	0·4211 (12)			10·0 (6)			
O(2')	0·5439 (15)	0·6804 (26)	0·3585 (12)			10·4 (6)			
O(3')	0·2904 (11)	0·4344 (20)	0·2308 (9)			7·4 (4)			
O(4')	0·2999 (11)	0·2310 (19)	0·2253 (9)			7·2 (4)			
O(5')	0·5698 (13)	0·0193 (23)	0·3552 (10)			9·4 (5)			
O(6')	0·6945 (14)	0·1147 (22)	0·4168 (11)			9·2 (5)			
O(7')	0·6972 (10)	0·3622 (17)	0·3691 (8)			6·2 (3)			
O(8')	0·6566 (9)	0·3513 (15)	0·4625 (7)			5·0 (2)			

was equal to about 0·7 times the corresponding σ. The R index* fell to 0·064 for the potassium compound and to 0·102 for the caesium salt; the observed and calculated structure factors are reported in Tables 2 and 3. The final parameters of the heavier atoms are given in Tables 4 and 5 and of the hydrogen atoms in Table 6.

Table 6. *Parameters for the hydrogen atoms in the potassium salt*

Atom	x	y	z	B
H(1)	0·9016	0·3905	0·3401	4·0
H(2)	0·9118	−0·0039	0·3694	4·0
H(3)	0·7070	0·1450	0·4245	4·0
H(4)	0·6779	0·2930	0·4708	4·0
H(5)	0·5900	0·2140	0·6200	4·5
H(6)	0·5500	0·1100	0·4350	4·5
H(7)	0·6200	0·0680	0·5750	4·5
H(8)	1·0408	0·4252	0·7427	4·0
H(9)	1·0368	0·2623	0·7139	4·0
H(10)	1·0350	0·3230	0·9800	4·5
H(11)	1·1380	0·3530	0·9308	4·5
H(12)	1·0700	0·4700	0·9700	4·5
H(1')	0·5502	0·0886	0·1465	4·0
H(2')	0·5589	0·4995	0·1523	4·0

(H(3') to H(7') not located)

H(8')	0·4500	0·3162	0·4036	4·0
H(9')	0·4055	0·4536	0·4279	4·0
H(10')	0·3300	0·2100	0·4730	4·5
H(11')	0·2850	0·3400	0·5150	4·5
H(12')	0·3900	0·3600	0·6100	4·5

Precision of the results

For the potassium salt, the standard deviations in co-ordinates, as derived from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle, correspond to positional uncertainties ranging from 0·003 to 0·005 Å for the oxygen atoms and about 0·005 Å for the nitrogen and the carbon atoms in the rings to about 0·01 Å for the terminal carbon atoms in the ethoxyl groups, and a maximum of 0·015 Å for the disordered ethoxyl group. The corresponding standard deviations in bond distances are about 0·007 Å for the rings and the nitro groups, about 0·012 Å for C–C bonds in ethoxyl groups, and up to 0·020 Å for the disordered chain. The standard deviations in bond angles range from 0·4° for O–C(1)–O and about 0·5° in the rings and the nitro groups up to 0·7° and 1·1° for O–C–C in 'normal' or disordered ethoxyl groups.

For the caesium salt, standard deviations in the co-ordinates of the lighter atoms are much higher, amounting to about 0·024 Å for the atoms in the rings and the

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* The values of the R index as here reported have been calculated omitting all the unobserved reflexions and the observed reflexions with zero weight (marked with an asterisk in Tables 2 and 3). In these calculations and in the least squares, atomic scattering factors for hydrogen were taken from Forsyth & Wells (1959) and for the heavier atoms from Cromer & Waber (1965).
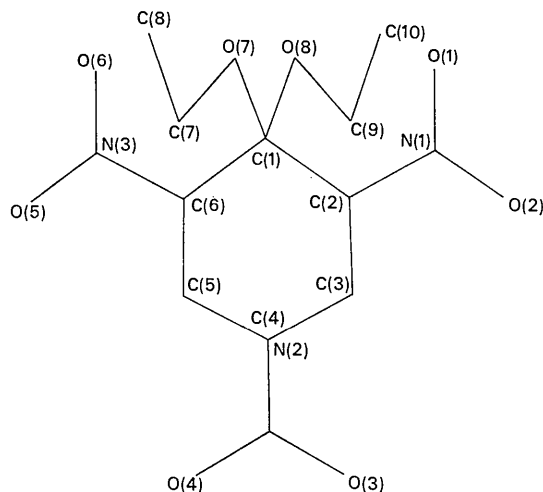

Fig. 2. Scheme of a molecule of Meisenheimer complex, showing numbering of atoms.
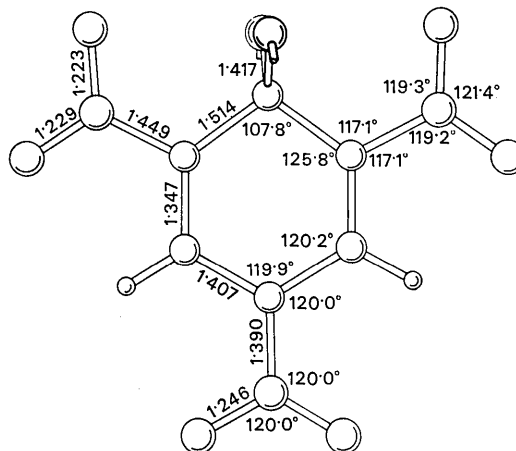

Fig. 3. Average of 'chemically equivalent' bond lengths and angles in the molecules of the potassium salt.
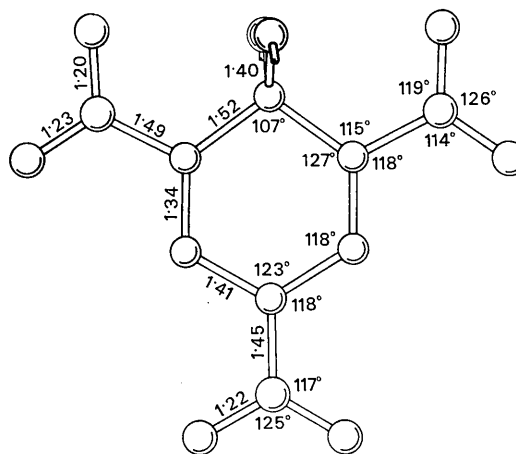

Fig. 4. Average of 'chemically equivalent' bond lengths and angles in the molecules of the caesium salt.

nitro groups and to about 0·040 Å for terminal carbon atoms in the ethoxyl groups. The standard deviations in bond distances range from 0·03 Å to 0·05 Å and in bond angles from 1·5° to about 2·5°.

No discussion about the precision of C–H bonds and angles is felt to be appropriate.

Discussion

The molecular structure

The molecules as viewed normal to the planes of the rings are shown in Figs. 3 and 4. Because of the far
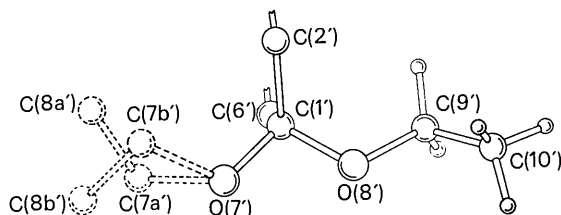

Fig. 5. Conformation of the ethoxyl groups (one of which is disordered) in one molecule of the potassium salt.

better precision attained with the potassium salt, a detailed discussion for the Cs compound does not seem justified beyond a description of the general shape of the molecule; unless otherwise specified, the numerical values here mentioned refer to the average of all the equivalent bond lengths and angles in the molecules of the K salt, when molecular symmetry $mm2$ is assumed.

An evident feature in all the molecules is the 'paraffinic' character of the carbon atom directly bonded to the ethoxyl group, which results in longer C–C bonds (1·514 Å) than in a phenyl ring and in a corresponding tetrahedral (107·8°) C–C–C angle. Another interesting feature is the presence of two short C–C bonds (1·347Å) in each ring.

All the rings are essentially planar, with a maximum deviation from the median plane of 0·026 Å in the case of the K salt (Table 7). The displacements, although small, exceed the probable error and seem to indicate some kind of distortion in the molecules; it is interesting to notice, however, that this distortion is not the same in the two molecules in the asymmetric unit.

The C–NO$_2$ groups are all essentially planar and not subjected to extensive rotation with respect to the plane

Table 7. Some planes of interest

The coefficients q_i are the direction cosines relative to the crystallographic axes **a**, **b** and **c**. Atoms omitted from the calculation of the least-squares plane are indicated with an asterisk; the remaining atoms were given equal weights.

(a) Potassium salt, first molecule.

Phenyl ring	Δ	1st nitro group	Δ	2nd nitro group	Δ	3rd nitro group	Δ	Ethoxyl group	Δ
C(1)	−0·026 Å	N(1)	−0·020 Å	N(2)	−0·009 Å	N(3)	0·003 Å	O(7)	(0·000 Å)
C(2)	0·023	O(1)	0·007	O(3)	0·003	O(5)	−0·001	O(8)	(0·000)
C(3)	0·000	O(2)	0·007	O(4)	0·003	O(6)	−0·001	C(1)	(0·000)
C(4)	−0·020	C(2)	0·006	C(4)	0·003	C(6)	−0·001	C(7)*	0·094
C(5)	0·014							C(8)*	−0·471
C(6)	0·010							C(9)*	−0·029
N(1)*	0·062							C(10)*	−0·320
N(2)*	−0·038								
N(3)*	0·037								

	q_1	q_2	q_3	D		Angle with phenyl ring
Phenyl ring	$q_1=0·8631$	$q_2=0·0272$	$q_3=0·1966$	$D=12·259$ Å		$=3·4°$
1st nitro group	0·8619	−0·0293	0·2277	12·213		0·3
2nd nitro group	0·8654	0·0237	0·1941	12·251		1·5
3rd nitro group	0·8547	0·0508	0·1990	12·204		89·9
Ethoxyl group	−0·1316	0·9989	−0·3143	−0·846		

(b) Potassium salt, second molecule.

Phenyl ring	Δ	4th nitro group	Δ	5th nitro group	Δ	6th nitro group	Δ	Ethoxyl group	Δ
C(1')	−0·012 Å	N(1')	0·000 Å	N(2')	0·011 Å	N(3')	−0·007 Å	O(7')	(0·000 Å)
C(2')	0·008	O(1')	0·000	O(3')	−0·004	O(5')	0·002	O(8')	(0·000)
C(3')	−0·003	O(2')	0·000	O(4')	−0·004	O(6')	0·002	C(1')	(0·000)
C(4')	0·002	C(2')	0·000	C(4')	−0·004	C(6')	0·002	C(7a')*	0·395
C(5')	−0·008							C(8a')*	−0·423
C(6')	0·013							C(7b')*	−0·403
N(1')*	0·042							C(8b')*	0·635
N(2')*	−0·056							C(9')*	0·104
N(3')*	0·037							C(10')*	−0·504

	q_1	q_2	q_3	D		Angle with the phenyl ring
Phenyl ring	$q_1=−0·0217$	$q_2=−0·0023$	$q_3=0·9270$	$D=1·211$ Å		$=5·8°$
4th nitro group	−0·1039	0·0667	0·9227	0·810		3·0
5th nitro group	0·0302	−0·0055	0·9132	1·620		3·0
6th nitro group	−0·0488	−0·0422	0·9450	0·912		3·0
Ethoxyl group	−0·0952	0·9995	−0·2705	1·868		89·5

Table 7 (cont.)

(c) Caesium salt, first molecule.

Phenyl ring	Δ	1st nitro group	Δ	2nd nitro group	Δ	3rd nitro group	Δ	Ethoxyl group	Δ
C(1)	0·01 Å	N(1)	0·01 Å	N(2)	−0·01 Å	N(3)	0·03 Å	O(7)	(0·00 Å)
C(2)	−0·01	O(1)	−0·00	O(3)	0·00	O(5)	−0·01	O(8)	(0·00)
C(3)	−0·01	O(2)	−0·00	O(4)	0·00	O(6)	−0·01	C(1)	(0·00)
C(4)	0·03	C(2)	−0·00	C(4)	0·00	C(6)	−0·01	C(7)*	0·06
C(5)	−0·03							C(8)*	0·03
C(6)	0·01							C(9)*	−0·03
N(1)*	−0·08							C(10)*	−0·13
N(2)*	0·05								
N(3)*	0·03								

	q_1	q_2	q_3	D	
Phenyl ring	0·9876	−0·0950	−0·2258	0·351 Å	
1st nitro group	0·9977	0·0541	−0·3856	−0·296	Angle with the phenyl ring = 13°
2nd nitro group	0·9864	−0·0770	−0·2064	0·479	2
3rd nitro group	0·9856	−0·1057	−0·2185	0·411	1
Ethoxyl group	0·0998	0·9945	−0·0643	0·906	90

(d) Caesium salt, second molecule.

Phenyl ring	Δ	4th nitro group	Δ	5th nitro group	Δ	6th nitro group	Δ	Ethoxyl group	Δ
C(1′)	−0·00 Å	N(1′)	0·06 Å	N(2′)	−0·04 Å	N(3′)	0·00 Å	O(7′)	(0·00 Å)
C(2′)	0·00	O(1′)	−0·02	O(3′)	−0·02	O(5′)	−0·00	O(8′)	(0·00)
C(3′)	−0·01	O(2′)	−0·02	O(4′)	−0·02	O(6′)	−0·00	C(1′)	(0·00)
C(4′)	0·01	C(2′)	−0·02	C(4′)	0·01	C(6′)	−0·00	C(7′)*	0·10
C(5′)	−0·01							C(8′)*	−0·84
C(6′)	0·01							C(9′)*	0·04
N(1′)*	0·04							C(10′)*	0·11
N(2′)*	−0·13								
N(3′)*	0·03								

	q_1	q_2	q_3	D	
Phenyl ring	−0·5822	−0·0625	0·9623	1·584 Å	
4th nitro group	−0·6001	−0·0262	0·9581	1·595	Angle with the phenyl ring = 2°
5th nitro group	−0·6287	−0·0917	0·9425	1·057	4
6th nitro group	−0·5852	−0·0450	0·9625	1·611	1
Ethoxyl group	−0·0391	0·9985	0·0484	3·743	90

of the ring. In the K salt, the maximum displacement from the median plane (0·020 Å) is observed for N(1) and the maximum dihedral angle between the median plane of a nitro group and the ring, observed for N(1′) and its neighbours, is slightly below 6°; in the Cs salt, the maximum displacement from the median plane, observed for N(1′), is greater (0·06 Å) and the maximum dihedral angle with the ring amounts to 13° (for the first nitro group).

By contrast, in the parent aromatic compound 2,4,6-trinitrophenetole, rotations up to 61·3° have been observed (Gramaccioli, Destro & Simonetta, 1967, 1968); a probable reason is the difference in the geometry of the ring carbon atom bonded to the ethoxyl groups. Whereas in trinitrophenetole the oxygen atom was forced to stay on the plane of the phenyl ring, between two nitro groups, here the tetrahedral arrangement of bonds around the corresponding carbon atoms keeps the oxygen atoms of the ethoxyl groups far away from the ring and coplanarity of nitro groups with the ring can be reached without any serious strain.

Another point of interest relative to the nitro groups is the evident non-equivalence between the groups situated opposite to the tetrahedral carbon atom and the others. This reflects in the shortening of the C(4)–N(2) bond (1·390 Å) with respect to the other two C–N bonds in the same molecule (1·449 Å); corresponding to this shortening, a lengthening of the N(4)–O bonds is observed (1·246 Å against 1·226 Å). All this is in evident agreement with theoretical considerations.

The C(1)–O bonds, which connect the ring to the ethoxyl groups, seem to be regular in length (1·417 Å), contrarily to the case of 2,4,6-trinitrophenetole, where the C(1)–O bond was much shorter (1·368 Å). Another interesting feature can be observed in the O–C(1)–O angles (Table 11) which are all close to their average value of 101·0°, even in the caesium salt. These angles are definitely smaller than the assumed value for the O–C–O angle in some ethers, such as 109·5° for methylal (Aoki, 1953). The O–C(1)–O plane is normal to the plane of the ring within the experimental error.

Examining now the ethoxyl groups, the most salient feature is the shortening of the terminal C–C bonds by an amount which exceeds the standard deviation by several times. A possible explanation consists in examining the thermal factors, whose anisotropy is definitely strong; here these distances and angles are

given uncorrected for these effects.* In the case of the disordered ethoxyl group, further complication may arise from the partial overlapping of the four 'half-carbons' in the structure and least-squares refinement for this part of the structure might not lead to perfectly correct results: from this point of view, the theoretical results (see below) may be superior.

Molecular orbital calculations

Molecular orbital calculations for 2,4,6-trinitrophenetole (20 π-electrons) and the complex obtained from it by addition of ethoxide anion (18 π-electrons) were performed for the carbon atoms in the Hückel approximation by use of the ω-technique (Streitwieser, 1961, p. 115). The variation of carbon–carbon β's with π-bond order (viz. bond length) was also included (Casalone, Mariani, Mugnoli & Simonetta, 1967). The necessary parameters for hetero-atoms were taken according to Streitwieser's suggestion (Streitwieser, 1961, p. 135). All nitro groups were taken as coplanar with the ring, except the groups in positions 2 and 6 of 2,4,6-trinitrophenetole, which were presumed to be rotated by 30° (Gramaccioli, Destro & Simonetta, 1967, 1968); as a consequence, the β_{C-N} values were assumed to be equal to β_0 $_{C-N}$ cos χ, where β_0 $_{C-N}$ is the value for parallel π-orbitals and χ is the angle of rotation of the nitro group. In the case of the Meisenheimer complex no inductive effect from the ethoxide groups was introduced.

Final charge densities and bond orders in the system of carbon atoms are shown in Table 8, together with the calculated bond lengths (Coulson, 1939). The agreement between theoretical and experimental C–C bond lengths is fair, although the calculations refer to an isolated molecule or anion.

These results are in essential agreement with similar Hückel molecular orbital calculations found in the literature (Caveng, Fischer, Heilbronner, Miller & Zollinger, 1967): in particular, the decrease in the electron charge of the ring after formation of the Meisenheimer complex is confirmed, the use of experimental geometry leading to a still stronger effect (5·64 π-electrons in the phenetole against 4·33 in the Meisenheimer complex).

Molecular packing

Assuming the set of van der Waals radii used in repulsion energy calculations (see above) and 1·2 Å for hydrogen, from Table 9 we see that in a very few cases two atoms belonging to a different molecule are situated at a smaller distance than the sum of the corresponding van der Waals radii: moreover, all the reported distances are only slightly below this value.

For the potassium salt, all the hydrogen atoms were considered separately, except in the case of the dis-

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* In general, it is well known that the distances between the 'atomic positions', as deduced from a crystal structure analysis, can be interpreted as real interatomic distances only in the limit of negligibly small thermal displacements (Busing & Levy, 1964).

Table 8. *Results from molecular orbital calculations*

(a) 2,4,6-trinitrophenetole

Atoms	Charge density (electrons)
C(1)	0·869
C(2) = C(6)	0·973
C(3) = C(5)	0·938
C(4)	0·948
N(1) = N(3)	1·556
N(2)	1·547
O(1) = O(2) = O(5) = O(6)	1·284
O(3) = O(4)	1·327

Bonds	Order (π)	Distance (calc).
C(1)–C(2) = C(1)–C(6)	0·576	1·415 Å
C(2)–C(3) = C(5)–C(6)	0·656	1·400
C(3)–C(4) = C(4)–C(5)	0·595	1·411

(b) Meisenheimer complex

Atoms	Charge density (electrons)
C(2) = C(6)	0·835
C(3) = C(5)	0·916
C(4)	0·827
N(1) = N(3)	1·544
N(2)	1·557
O(1) = O(2) = O(5) = O(6)	1·508
O(3) = O(4)	1·497

Bonds	Order (π)	Distance (calc.)
C(2)–C(3) = C(5)–C(6)	0·727	1·387 Å
C(3)–C(4) = C(4)–C(5)	0·531	1·423

Table 9. *Intermolecular contact distances*

(a) Potassium salt

C(5)——C(8b')	$1-x,\ -y,\ -z$	3·48 Å
C(5')——H(12')	$1-x, 1-y, 1-z$	2·78
C(10')–C(8b')	$x,\ y, z+1$	3·53
O(5) —C(8b')	$1-x,\ -y,\ -z$	3·26
O(5')–H(5)	$1-x, 1-y, 1-z$	2·56
C(7a')–H(11)	$x-1,\ y, z-1$	2·81
C(8a')–H(3)	$1-x,\ -y,\ -z$	3·05
C(8a')–H(1')	$1-x,\ -y,\ -z$	3·07
C(8b')–H(2)	$1-x,\ -y,\ -z$	2·94
C(8b')–H(11)	$x-1,\ y, z-1$	2·92
H(12) –H(12)	$2-x, 1-y, 2-z$	2·39
H(2')——H(12')	$1-x, 1-y, 1-z$	2·30

(b) Caesium salt

C(8)——C(8)	$1-x,\ -y, 1-z$	3·85 Å
C(10)–C(8')	$x-1,\ y,\ z$	3·97
C(8') –C(10')	$x, \frac{1}{2}-y, z-\frac{1}{2}$	3·82

ordered ethoxyl group, where radii for the whole methylene and methyl groups were assumed; for the caesium salt, owing to the experimental impossibility of locating most of the hydrogen atoms, the latter criterion was applied to all the ethoxyl groups. The molecular packing of the two substances is represented in Figs. 6 and 7.

The most significant distances between the cations and adjacent atoms are shown in Table 10. It is to be noticed that all these nearest neighbours, except one nitrogen for each Cs$^+$ ion, are oxygen atoms; this is to be expected for the minimization of Coulomb interaction energy (see Table 8). It appears that there is no regular polyhedron surrounding the metal ions.

After the shifts of neighbouring atoms due to the final cycles of least squares, one might question whether the situation around the disordered ethoxyl group remains actually the same as it was found during the previous stage of the refinement. In order to check this possibility, the interaction energy between non-bonded atoms was again evaluated as a function of the angles of rotation φ_1 and φ_2, using the final co-
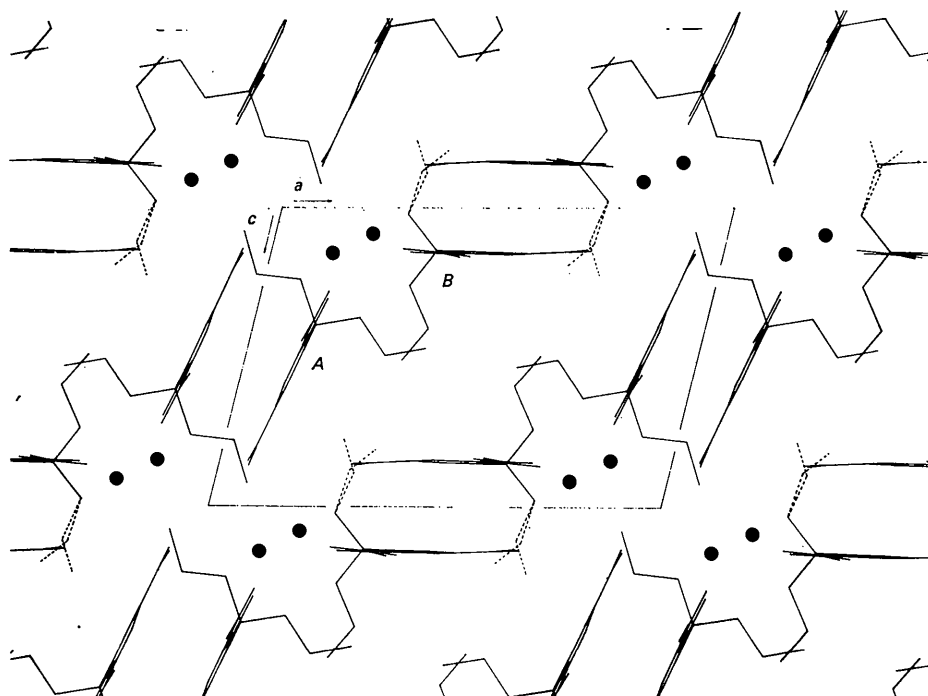

Fig. 6. Molecular packing in the potassium salt, seen along b. The black circles indicate the positions of the cations.
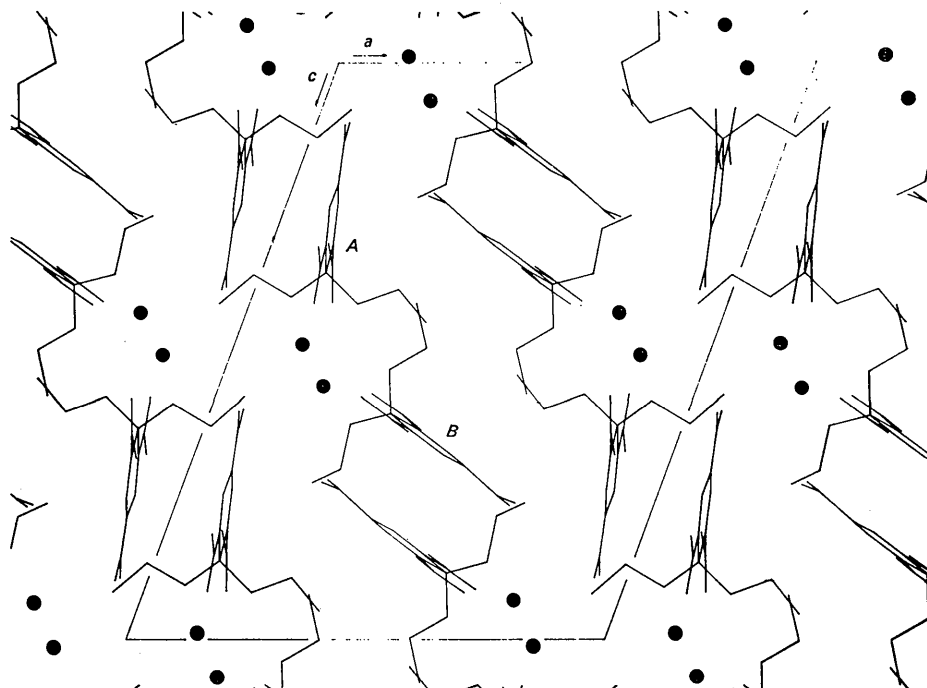

Fig. 7. Molecular packing in the caesium salt, seen along b. The black circles indicate the positions of the cations.

Table 10. *Distances from the cation*

(a) Potassium (below 3·2 Å)

K(1)–O(3)	transl.	x,	y,	$z+1$	2·902 Å
–O(6)					2·959
–O(7)					2·706
–O(8)					2·883
–O(1')	transl.	$1-x$,	$-y$,	$1-z$	2·798
–O(3')	transl.	x,	y,	$1+z$	3·068
–O(4')	transl.	x,	y,	$1+z$	2·951
–O(6')	transl.	$1-x$,	$1-y$,	$1-z$	2·855
K(2)–O(1)	transl.	$1-x$,	$1-y$,	$1-z$	2·939 Å
–O(3)	transl.	$x-1$,	y,	z	3·131
–O(4)	transl.	$x-1$,	y,	z	3·107
–O(4)	transl.	$1-x$,	$-y$,	$-z$	2·959
–O(6)	transl.	$1-x$,	$-y$,	$1-z$	2·832
–O(1')					2·939
–O(7')					2·848
–O(8')					2·709

(b) Caesium (below 3·5 Å)

Cs(1)–N(2')					3·38 Å
–O(1)	transl.	x,	$\frac{1}{2}-y$,	$z-\frac{1}{2}$	3·46
–O(3)					3·14
–O(7)	transl.	x,	$\frac{1}{2}-y$,	$z-\frac{1}{2}$	2·99
–O(8)	transl.	x,	$\frac{1}{2}-y$,	$z-\frac{1}{2}$	3·11
–O(1')	transl.	$1-x$,	$y-\frac{1}{2}$,	$\frac{1}{2}-z$	3·06
–O(3')					3·23
–O(4')					3·23
–O(8')	transl.	$1-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$	3·10
Cs(2)–N(2)	transl.	$1+x$,	y,	z	3·41 Å
–O(1)	transl.	$1-x$,	$y-\frac{1}{2}$,	$\frac{1}{2}-z$	3·07
–O(3)	transl.	$1+x$,	y,	z	3·32
–O(4)	transl.	$1+x$,	y,	z	3·28
–O(4)	transl.	$1-x$,	$-y$,	$-z$	3·20
–O(6)	transl.	$1-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$	3·18
–O(1')	transl.	x,	$\frac{1}{2}-y$,	$z-\frac{1}{2}$	3·48
–O(7')	transl.	x,	$\frac{1}{2}-y$,	$z-\frac{1}{2}$	3·08
–O(8')	transl.	x,	$\frac{1}{2}-y$,	$z-\frac{1}{2}$	2·99

ordinates for all the atoms, except C(7') and C(8'), whose positions were chosen as in the previous calculations.* The results obtained clearly show that no substantial change has occurred, the 'new' points of minimum being almost coincident with the 'old' ones. During these final calculations, the difference in energy between the various models was also accounted for by adding the energies for C(7')–C(8') bond stretching and bond angle bending [C(1')–O(7')–C(7') and O(7')–C(7')–C(8')]. The strains associated with a change of bond length r or bond angle θ from their equilibrium values were obtained by the expressions: $E_s = 0·5\ k_s(r-r_e)^2$ and $E_b = 0·5\ k_b(\theta-\theta_e)^2$, respectively. The following values were assigned to the necessary parameters: for C–C, $k_s = 5·10^5$ dyne.cm^{-1}, $r_e = 1·533$ Å (Gleicher & Schleyer, 1967); for C–O–C, $k_b = 65·10^{-13}$ erg.rad^{-2}, $\theta_e = 111°$; for O–C–C, $k_b = 36·10^{-12}$ erg.rad^{-2}, $\theta_e = 110°$. Of these, the θ_e values are consistent with figures found in the literature (Kimura & Kubo, 1951; Kimura, 1950), while the bending force constants have

* Here, as before, each model was characterized by a certain value for the C(7')–C(8') bond length (1·52, 1·53 or 1·54 Å) and by either 110° or 115° for the angles C(1')–O(7')–C(7') and O(7')–C(7')–C(8'): it was therefore assumed that the real molecular geometry is not far from a 'regular' situation.

been evaluated from spectroscopic data (Herzberg, 1945).

For the K salt, the model corresponding to the absolute minimum points was characterized by the following parameters: C(7')–C(8') = 1·53 Å (experimental = 1·47 and 1·38 Å), C(1')–O(7')–C(7') angle = 115° (experimental = 113° and 120°) and O(7')–C(7')–C(8') angle = 110° (experimental = 107° and 118°). The angular coordinates φ_1 and φ_2 were equal to $-50°$ and $-10°$ in one case (experimental values at the end of the refinement = $-51·9°$ and $-17·1°$) and to $+80°$ and $+20°$ in the other (experimental values = $+112·5°$ and $+18°$). The difference in energy between the two minima was as low as 0·18 kcal.mole^{-1}; this completely explains our observation of approximately equal population.

For the Cs salt, the absolute minimum was found for the model with C(7')–C(8') = 1·53 Å (experimental = 1·37 Å), C(1')–O(7')–C(7') = 115° (experimental = 115·5°) and O(7')–C(7')–C(8') = 110° (experimental = 112°). The corresponding angular coordinates φ_1 and φ_2 are respectively $-50°$ (experimental = $-48·9°$) and $0°$ (experimental = $+4·4°$). As in the previous calculations, the virtual absence of disorder was confirmed, the energy of the next point of minimum being higher by about 1 kcal.mole^{-1}.

Since the experimental geometry in the disordered ethoxyl group is rather unsatisfactory, the reliability of the 'theoretical' results was checked by calculating the corresponding structure factors and R index, assuming isotropic thermal factors for the four atoms C(9a'), C(10a'), C(9b') and C(10b'). For each atom, thermal factors were obtained by geometrical averaging of the three B's along the principal axes of thermal vibration ellipsoid. As a result, a value of 0·087 was obtained for the R index (for all reflexions, except 'less than'), which is to be compared with the R index of 0·073, calculated for the experimental geometry in the same conditions. For the caesium salt, the corresponding values of R are 0·108 ('theoretical') and 0·107 (experimental).

For the potassium compound, the conformations of the methyl groups, whose positions could be derived experimentally, are respectively staggered for C(10'), eclipsed for C(8) and half way between for C(10). In order to obtain a possible explanation of this fact, the non-bonded interaction energy between the hydrogen atoms in the methyl groups and the surrounding atoms has been evaluated as a function of the angle of rotation around the C–C bonds to the adjacent methylenes: for this purpose the expression (1) was still used. It was found that the minimum of repulsion energy occurs in coincidence with the experimental situation; the energy differences between minima and maxima are however very low (0·15 to 0·20 kcal.mole^{-1}).

Since in molecules like ethane and n-butane interatomic repulsions are not the only factor giving rise to torsional energy, but account for approximately one third of it (Allinger, Miller, Van Catledge & Hirsch,

Table 11. *Intramolecular distances and angles*

(Uncorrected for thermal libration)

(*a*) Potassium salt

1st molecule		2nd molecule	
C(1)–C(2)	1·516 Å	C(1')—C(2')	1·515 Å
C(2)–C(3)	1·354	C(2')—C(3')	1·352
C(3)–C(4)	1·404	C(3')—C(4')	1·406
C(4)–C(5)	1·406	C(4')—C(5')	1·414
C(5)–C(6)	1·347	C(5')—C(6')	1·335
C(6)–C(1)	1·512	C(6')—C(1')	1·512
C(2)–N(1)	1·452	C(2')—N(1')	1·444
C(4)–N(2)	1·387	C(4')—N(2')	1·392
C(6)–N(3)	1·454	C(6')—N(3')	1·447
N(1)–O(1)	1·212	N(1')—O(1')	1·233
N(1)–O(2)	1·229	N(1')—O(2')	1·230
N(2)–O(3)	1·256	N(2')—O(3')	1·253
N(2)–O(4)	1·243	N(2')—O(4')	1·234
N(3)–O(5)	1·221	N(3')—O(5')	1·236
N(3)–O(6)	1·221	N(3')—O(6')	1·226
C(1)–O(7)	1·410	C(1')—O(7')	1·416
C(1)–O(8)	1·425	C(1')—O(8')	1·417
O(8)–C(9)	1·440	O(8')—C(9')	1·425
C(9)–C(10)	1·412	C(9')—C(10')	1·447
O(7)–C(7)	1·415	O(7')—C(7a')	1·478
		O(7')—C(7b')	1·489
C(7)–C(8)	1·444	C(7a')–C(8a')	1·381
		C(7b')–C(8b')	1·477
C(6)–C(1)–C(2)	108·2°	C(6')–C(1')—C(2')	107·5°
C(1)–C(2)–C(3)	125·1	C(1')–C(2')—C(3')	126·5
C(2)–C(3)–C(4)	120·7	C(2')–C(3')—C(4')	119·4
C(3)–C(4)–C(5)	119·9	C(3')–C(4')—C(5')	119·9
C(4)–C(5)–C(6)	120·3	C(4')–C(5')—C(6')	120·7
C(5)–C(6)–C(1)	125·8	C(5')–C(6')—C(1')	125·9
C(1)–C(2)–N(1)	117·1	C(1')–C(2')—N(1')	117·0
C(3)–C(2)–N(1)	117·8	C(3')–C(2')—N(1')	116·4
C(2)–N(1)–O(1)	119·5	C(2')–N(1')—O(1')	119·6
C(2)–N(1)–O(2)	118·4	C(2')–N(1')—O(2')	120·1
O(1)–N(1)–O(2)	121·9	O(1')–N(1')—O(2')	120·3
C(3)–C(4)–N(2)	120·5	C(3')–C(4')—N(2')	120·2
C(5)–C(4)–N(2)	119·6	C(5')–C(4')—N(2')	119·9
C(4)–N(2)–O(3)	119·1	C(4')–N(2')—O(3')	119·5
C(4)–N(2)–O(4)	120·6	C(4')–N(2')—O(4')	120·6
O(3)–N(2)–O(4)	120·2	O(3')–N(2')—O(4')	119·9
C(5)–C(6)–N(3)	116·9	C(5')–C(6')—N(3')	117·2
C(1)–C(6)–N(3)	117·3	C(1')–C(6')—N(3')	116·9
C(6)–N(3)–O(5)	119·5	C(6')–N(3')—O(5')	118·8
C(6)–N(3)–O(6)	119·1	C(6')–N(3')—O(6')	119·1
O(5)–N(3)–O(6)	121·4	O(5')–N(3')—O(6')	122·1
O(7)–C(1)–C(6)	111·1	O(7')–C(1')—C(6')	113·0
O(8)–C(1)–C(2)	112·0	O(8')–C(1')—C(2')	110·9
O(7)–C(1)–C(2)	112·4	O(7')–C(1')—C(2')	112·7
O(8)–C(1)–C(6)	111·7	O(8')–C(1')—C(6')	112·4
O(7)–C(1)–O(8)	101·4	O(7')–C(1')—O(8')	100·4
C(1)–O(8)–C(9)	115·0	C(1')–O(8')—C(9')	116·0
O(8)–C(9)–C(10)	110·7	O(8')–C(9')—C(10')	110·7
C(1)–O(7)–C(7)	116·5	C(1')–O(7')—C(7a')	120·1
		C(1')–O(7')—C(7b')	113·0
O(7)–C(7)–C(8)	111·6	O(7')–C(7a')–C(8a')	118·5
		O(7')–C(7b')–C(8b')	107·6

(*b*) Caesium salt

1st molecule		2nd molecule	
C(1)–C(2)	1·49 Å	C(1')–C(2')	1·51 Å
C(2)–C(3)	1·36	C(2')–C(3')	1·38
C(3)–C(4)	1·37	C(3')–C(4')	1·39
C(4)–C(5)	1·45	C(4')–C(5')	1·42
C(5)–C(6)	1·31	C(5')–C(6')	1·30
C(6)–C(1)	1·51	C(6')–C(1')	1·56
C(2)–N(1)	1·55	C(2')–N(1')	1·46
C(4)–N(2)	1·45	C(4')–N(2')	1·45
C(6)–N(3)	1·45	C(6')–N(3')	1·51

Table 11 (cont.)

1st molecule		2nd molecule	
N(1)–O(1)	1·20	N(1′)–O(1′)	1·23
N(1)–O(2)	1·23	N(1′)–O(2′)	1·19
N(2)–O(3)	1·21	N(2′)–O(3′)	1·22
N(2)–O(4)	1·24	N(2′)–O(4′)	1·20
N(3)–O(5)	1·26	N(3′)–O(5′)	1·24
N(3)–O(6)	1·20	N(3′)–O(6′)	1·18
C(1)–O(7)	1·43	C(1′)–O(7′)	1·39
C(1)–O(8)	1·39	C(1′)–O(8′)	1·41
O(8)–C(9)	1·42	O(8′)–C(9′)	1·40
C(9)–C(10)	1·48	C(9′)–C(10′)	1·51
O(7)–C(7)	1·40	O(7′)–C(7′)	1·51
C(7)–C(8)	1·43	C(7′)–C(8′)	1·37

1st molecule		2nd molecule	
C(6)–C(1)–C(2)	108ᵛ	C(6′)–C(1′)–C(2′)	106°
C(1)–C(2)–C(3)	130	C(1′)–C(2′)–C(3′)	126
C(2)–C(3)–C(4)	114	C(2′)–C(3′)–C(4′)	119
C(3)–C(4)–C(5)	124	C(3′)–C(4′)–C(5′)	122
C(4)–C(5)–C(6)	119	C(4′)–C(5′)–C(6′)	118
C(5)–C(6)–C(1)	125	C(5′)–C(6′)–C(1′)	129
C(1)–C(2)–N(1)	114	C(1′)–C(2′)–N(1′)	117
C(3)–C(2)–N(1)	117	C(3′)–C(2′)–N(1′)	118
C(2)–N(1)–O(1)	119	C(2′)–N(1′)–O(1′)	116
C(2)–N(1)–O(2)	114	C(2′)–N(1′)–O(2′)	116
O(1)–N(1)–O(2)	127	O(1′)–N(1′)–O(2′)	126
C(3)–C(4)–N(2)	118	C(3′)–C(4′)–N(2′)	118
C(5)–C(4)–N(2)	118	C(5′)–C(4′)–N(2′)	119
C(4)–N(2)–O(3)	118	C(4′)–N(2′)–O(3′)	116
C(4)–N(2)–O(4)	118	C(4′)–N(2′)–O(4′)	117
O(3)–N(2)–O(4)	124	O(3′)–N(2′)–O(4′)	126
C(5)–C(6)–N(3)	118	C(5′)–C(6′)–N(3′)	119
C(1)–C(6)–N(3)	117	C(1′)–C(6′)–N(3′)	112
C(6)–N(3)–O(5)	117	C(6′)–N(3′)–O(5′)	111
C(6)–N(3)–O(6)	119	C(6′)–N(3′)–O(6′)	123
O(5)–N(3)–O(6)	124	O(5′)–N(3′)–O(6′)	126
O(7)–C(1)–C(6)	111	O(7′)–C(1′)–C(6′)	112
O(8)–C(1)–C(2)	113	O(8′)–C(1′)–C(2′)	112
O(7)–C(1)–C(2)	112	O(7′)–C(1′)–C(2′)	114
O(8)–C(1)–C(6)	113	O(8′)–C(1′)–C(6′)	111
O(7)–C(1)–O(8)	100	O(7′)–C(1′)–O(8′)	101
C(1)–O(8)–C(9)	115	C(1′)–O(8′)–C(9′)	117
O(8)–C(9)–C(10)	110	O(8′)–C(9′)–C(10′)	108
C(1)–O(7)–C(7)	116	C(1′)–O(7′)–C(7′)	116
O(7)–C(7)–C(8)	110	O(7′)–C(7′)–C(8′)	112

1967; Harada & Shimanouchi, 1967), the 'pure' torsional barrier for situations of this kind can be estimated at about 2 kcal.mole⁻¹, with the consequence that torsional forces should predominate in our case. A possible explanation for this discrepancy could consist in the fact that repulsion energy between non-bonded atoms had been underestimated in our calculations. As a matter of fact, when the 'harder' Williams potential function (Williams, 1966) is used for H–H interactions, repulsion energy barriers are found of the right order of magnitude (up to 4 kcal.mole⁻¹) and the experimental conformation is justified.

Thermal vibrations

The lengths and direction cosines of the principal axes of thermal vibration are given in Table 12. A marked anisotropy is evident for the terminal carbon atoms of the ethoxyl groups. Rather less marked, but always strong, is the anisotropy of thermal motion of all the oxygen atoms in the nitro groups; in this respect, their behaviour is clearly different from the oxygen atoms in the ethoxyl groups, as expected.

In general, the directions of maximum motion of the highly anisotropic atoms do not show a simple relation to the geometry of the molecules, except for a few cases, such as for O(1) and O(4′), where they form angles of 8° and 1°, respectively, with the normal to the plane of the corresponding nitro group.

In the ethoxyl groups, the principal thermal motions of the oxygen and the carbon atoms (except the 'disordered' C's) form angles ranging from 4° to 20° with the normal to the corresponding plane O–C(1)–O or O–C(1′)–O.

In conclusion, it seems to us that the structure of the intermediates in nucleophilic aromatic substitution reactions, as predicted on theoretical grounds (Wheland, 1942) and supported by kinetic results (Fendler, 1966), together with nuclear magnetic resonance spectroscopy experiments (Servis, 1967), is completely confirmed by X-ray diffraction.

Table 12. *Magnitudes and direction cosines, relative to the crystallographic axes, of the principal axes of the thermal vibration ellipsoids*

(a) Potassium salt

Atom	B_i	q_i^a	q_i^b	q_i^c
K(1)	3.56	0.850	0.007	0.232
	2.59	0.349	-0.890	-0.180
	2.18	0.395	0.456	-0.956
K(2)	3.66	0.004	0.127	0.872
	2.79	0.528	-0.901	0.228
	2.32	0.849	0.414	-0.433
C(1)	2.85	0.211	0.852	0.059
	2.22	0.604	-0.523	0.596
	1.60	0.769	0.015	0.801
C(2)	3.22	0.321	0.538	-0.944
	2.64	0.574	0.431	0.297
	1.99	0.753	-0.724	-0.146
C(3)	3.62	0.194	-0.946	-0.051
	2.60	0.845	-0.109	0.288
	1.80	0.498	0.304	-0.956
C(4)	3.46	0.009	-0.985	0.182
	2.81	0.848	-0.166	0.297
	1.99	0.529	0.049	-0.937
C(5)	3.47	0.295	0.872	-0.604
	2.91	0.201	0.194	0.762
	2.02	0.934	-0.450	-0.233
C(6)	3.46	0.502	0.265	0.513
	2.69	0.590	0.468	-0.858
	2.24	0.633	-0.843	0.009
C(7)	6.90	0.083	-0.993	0.180
	3.41	0.651	0.057	-0.888
	2.21	0.755	-0.105	0.424
C(8)	13.24	0.443	-0.932	0.021
	4.39	0.504	0.322	-0.951
	3.22	0.741	0.169	0.308
C(9)	10.29	0.161	-0.994	0.170
	3.55	0.307	0.107	-0.985
	2.50	0.938	0.003	0.035
C(10)	11.76	0.040	0.986	-0.326
	8.43	0.624	-0.111	-0.860
	2.68	0.780	-0.122	0.394
N(1)	4.65	0.265	0.069	-0.978
	3.96	0.944	0.057	-0.026
	2.28	0.197	-0.996	0.206
N(2)	5.75	0.197	-0.991	0.150
	2.88	0.547	-0.051	0.632
	2.71	0.814	0.122	-0.760
N(3)	4.97	0.119	-0.371	-0.770
	2.89	0.938	0.227	-0.347
	2.54	0.326	-0.900	0.534
O(1)	8.12	0.917	0.022	0.081
	5.89	0.202	0.623	-0.921
	2.63	0.345	-0.782	-0.381
O(2)	9.90	0.473	0.067	0.648
	5.91	0.880	-0.139	-0.641
	2.64	0.034	-0.988	0.412
O(3)	7.26	0.026	-0.921	-0.072
	4.55	0.860	-0.279	0.285
	2.15	0.509	0.273	-0.956
O(4)	7.39	0.287	0.881	-0.585
	5.53	0.808	-0.192	0.368
	2.47	0.515	-0.432	-0.723
O(5)	7.02	0.657	0.014	0.499
	5.46	0.732	0.063	-0.836
	2.25	0.180	-0.998	0.229
O(6)	8.17	0.544	0.321	0.430
	4.57	0.764	-0.688	-0.227
	2.37	0.348	0.650	-0.874
O(7)	3.98	0.054	-0.986	0.150
	2.34	0.002	0.150	-0.957
	1.94	0.999	-0.071	-0.249
O(8)	3.69	0.181	-0.998	0.247
	2.57	0.972	0.058	-0.429
	2.37	0.149	-0.003	0.869
C(1')	2.88	0.789	0.499	-0.259
	2.18	0.613	-0.326	-0.131
	2.00	0.044	-0.264	0.957
C(2')	3.29	0.826	-0.028	0.291
	2.62	0.538	0.122	-0.945
	1.95	0.168	-0.992	0.151
C(3')	3.28	-0.517	0.719	-0.063
	2.58	0.581	-0.675	0.544
	2.02	0.629	-0.166	-0.837
C(4')	3.20	0.089	0.976	-0.290
	2.58	0.233	-0.058	0.855
	1.56	0.968	-0.197	-0.430
C(5')	3.58	0.736	-0.291	0.478
	2.67	0.266	0.924	-0.362
	2.00	0.623	-0.249	-0.800
C(6')	3.22	0.262	-0.122	0.848
	2.41	0.151	0.961	-0.292
	2.04	0.953	-0.249	-0.442
C(7'a)	6.03	0.841	0.343	-0.618
	5.00	0.536	-0.671	0.595
	1.42	0.081	-0.657	-0.514
C(7'b)	11.79	0.736	0.580	-0.384
	3.19	0.516	-0.624	0.641
	1.44	0.437	-0.524	-0.665
C(8'a)	12.85	0.245	0.923	-0.476
	5.42	0.812	-0.228	0.367
	2.00	0.530	-0.311	0.800
C(8'b)	15.74	0.999	-0.111	-0.199
	5.00	0.052	-0.509	-0.649
	3.27	0.015	0.853	-0.734
C(9')	8.01	0.094	-0.985	0.437
	3.64	0.993	-0.019	-0.219
	2.81	0.076	-0.174	-0.873
C(10')	17.20	0.443	-0.941	0.093
	5.93	0.879	0.302	-0.125
	3.15	0.175	0.151	-0.988
N(1')	4.53	0.654	-0.159	0.557
	2.90	0.755	0.021	-0.813
	2.57	0.037	-0.987	0.170
N(2')	4.34	0.120	0.969	-0.363
	3.07	0.341	-0.053	0.786
	2.30	0.932	-0.239	-0.501
N(3')	4.20	0.742	-0.007	0.406
	3.08	0.665	-0.052	-0.857
	2.67	0.085	-0.999	0.317
O(1')	8.19	0.370	-0.303	0.810
	3.21	0.701	-0.635	-0.416
	2.48	0.609	0.711	-0.412
O(2')	5.87	0.867	-0.076	-0.678
	5.61	0.488	0.095	0.624
	2.36	0.105	-0.993	0.388
O(3')	5.39	0.202	0.884	-0.012
	4.74	0.036	0.338	-0.978
	2.65	0.979	-0.322	-0.209
O(4')	6.10	0.042	-0.027	0.916
	5.13	0.445	-0.943	0.131
	2.43	0.894	0.332	-0.379
O(5')	7.16	0.488	-0.037	0.677
	5.67	0.867	-0.032	-0.692
	2.28	0.104	-0.999	0.251
O(6')	7.25	0.266	0.189	0.730
	4.17	0.531	0.706	-0.677
	2.33	0.805	-0.683	-0.097
O(7')	4.00	0.073	-0.965	0.516
	2.61	0.907	0.057	0.080
	2.52	0.414	-0.257	-0.853
O(8')	3.71	0.262	-0.945	0.488
	2.69	0.682	0.303	0.283
	1.80	0.683	-0.122	-0.826

(b) Cesium salt

Atom	B_i	q_i^a	q_i^b	q_i^c
Cs(1)	6.47	0.961	-0.190	-0.524
	4.44	0.225	0.960	0.079
	3.64	0.163	-0.206	0.848
Cs(2)	6.06	0.677	0.243	-0.887
	4.56	0.254	-0.963	-0.171
	3.87	0.691	0.117	0.429

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