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Crystal chemistry study on nitrobenzenes Part 1. Molecular conformation and packing

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CRYSTAL CHEMISTRY STUDY ON NITROBENZENES §

PART 1. MOLECULAR CONFORMATION AND PACKING

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ABSTRACT

Based on 79 crystal structures of nitrobenzenes, the geometry of the benzene ring and the conformation of the nitro group were examined. The bond lengths and the endocyclic angles in the nearly planar benzene ring vary considerably, with the latter being well correlated to the electronic properties of the subtituents. Packing energy was calculated and consistent well with experimental value.

INTRODUCTION

§ Part of this work was done at Max-Planck Institut fuer Kohlenforschung a. d. Ruhr, Germany, on an occasion of a sabbatical leave. Many thanks are due to the local people there.

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Nitrobenzenes are an important class of explosives. Their properties are originated from their internal structures. To study the structure-property relationship systematically, a search was done on the crystal structures with the following criteria. In the molecule, 1). there is one and only one benzene ring and no other ring. 2). there is at least a NO_2 group directly attached to the benzene ring. 3). there is no other element than C, H, N, O, F, Cl, Br, I. In addition, the structure is full-determined and disorder-free. Structures containing carboxy group and complicated structures were intentionally excluded so that the attention could be focused on the NO_2 group and its functions on molecular packing. The database contains 79 structures, in which there are a total of 175 NO_2 groups. The database is not inclusive, but it is believed to be large enough to show the characteristics concerned in this communication.

GEOMETRY OF BENZENE RING

The geometrical calculation was summerized in table 1. As shown by the table the benzene ring is essentially planar. The average and maximum deviations from the ring plane for the ring atoms are 0.01Å and 0.09Å, respectively. The sum of the six internal angles is always equal to 360° within 2° , showing the substitution of NO_2 group has no signicant effect on the pla-

Table 1 Geometry of Benzene Ring in Nitrobenzenes*

NO.	Groups	S.G.	α_1	α_2	α_3	α_4	α_5	α_6	d_{61}	d_{12}	d_{23}	d_{34}	d_{45}	d_{56}
			h_1	h_2	h_3	h_4	h_5	h_6						
1	N M N C	P-1	123	114	124	119	119	121	1386	1395	1383	1395	1382	1360
			0	1	0	0	1	0						
2	N M N C M	$Pna2_1$	124	112	126	119	117	122	1350	1432	1358	1393	1396	1379
			0	-1	1	0	-2	2						
3	N N	$Pbn2_1$	123	116	124	118	120	119	1370	1371	1372	1374	1385	1374
			2	0	-3	3	-1	-1						
4	N N	$P2_1/n$	123	118	118	123	118	118	1377	1376	1387	1377	1377	1387
			0	0	0	0	0	0						
5	N M N M N T	$P2_1/a$	127	115	125	115	126	112	1400	1400	1390	1370	1400	1400
			0	-1	1	0	0	0						
6	N M M M N T	$P2_1/n$	126	118	119	118	127	110	1400	1397	1381	1390	1328	1395
			-1	0	2	-1	0	2						
7	N N M M M M	P-1	122	122	117	121	121	117	1389	1384	1380	1403	1401	1409
			1	1	0	1	-1	1						
8	N N N N N N	I2/c	119	122	118	119	118	122	1344	1406	1394	1398	1394	1406
			3	0	-4	4	0	-3						
9	N M	Pcab	123	117	123	117	121	119	1351	1408	1382	1388	1404	1383
			1	0	0	0	0	0						
10	N	$P2_1/c$	125	116	121	121	120	117	1358	1376	1405	1374	1447	1350
			1	3	-2	0	2	-1						
11	N M M M M M	P1	126	118	121	118	122	115	1405	1355	1365	1435	1411	1384
			1	0	1	1	0	1						
12	N M N M M M	$P2_1/n$	126	113	125	118	120	117	1380	1380	1390	1380	1390	1400
			0	0	0	0	0	0						
			125	114	125	118	120	118	1400	1380	1380	1390	1400	1390
			0	0	0	0	0	0						
13	N N N	Pbca	124	116	123	116	124	116	1375	1384	1374	1385	1381	1380
			2	-2	0	2	-3	1						
			122	119	123	115	124	117	1385	1374	1365	1363	1391	1385
			1	0	0	0	0	-1						
14	N M N N M	Pbcn	127	114	122	119	122	114	1384	1384	1394	1375	1375	1394
			0	1	-1	0	1	-1						
15	N N	$P2_1/c$	120	120	119	120	121	119	1376	1384	1376	1381	1374	1387
			1	0	0	-1	1	0						
16	N N N M	$Pca2_1$	123	119	121	116	126	114	1408	1372	1375	1415	1364	1390
			-3	1	1	1	-3	1						
			126	115	124	116	125	113	1379	1387	1373	1344	1383	1395
			1	-1	-1	2	-2	0						
17	N A N A N V	$P2_1/n$	122	117	122	116	123	119	1397	1435	1429	1437	1429	1377
			-8	3	5	-9	5	4						
18	N A N A N F	Pc	121	116	123	117	120	123	1379	1441	1440	1424	1425	1382
			0	1	-2	1	1	1						
19	N U B	$P2_1/c$	122	121	118	121	122	116	1388	1373	1370	1362	1398	1375
			1	-1	1	-1	0	0						
20	N C A	$Pna2_1$	123	117	123	117	122	118	1386	1401	1396	1394	1420	1392
			1	-2	2	-1	0	-1						
21	N A N	$P2_1/n$	123	113	123	121	119	121	1378	1429	1426	1389	1377	1378
			0	1	-1	0	0	0						
22	N A N A N	Pc	124	116	121	116	124	119	1375	1386	1467	1472	1392	1379
			-1	1	-2	2	-1	1						

Table 1 (continued)

NO.	Groups	S.G.	α_1	α_2	α_3	α_4	α_5	α_6	d_{61}	d_{12}	d_{23}	d_{34}	d_{45}	d_{56}
			h_1	h_2	h_3	h_4	h_5	h_6						
23	N S	$P2_1$	121	119	121	117	121	121	1386	1408	1379	1457	1407	1365
			1	1	-1	1	1	-1						
24	N X	$P2_1/n$	122	116	121	121	119	120	1395	1400	1405	1372	1379	1370
			0	0	0	0	0	0						
25	N N W	$P2_1/c$	122	118	121	120	120	120	1374	1380	1377	1382	1383	1364
			1	0	-1	1	0	-1						
			123	117	122	119	120	119	1375	1389	1371	1386	1394	1366
			0	0	0	0	0	0						
26	N N N W	$P2_1/c$	122	118	124	116	123	117	1402	1378	1372	1383	1390	1391
			-1	1	0	1	1	0						
27	N M N S	$P2_1/c$	121	115	126	115	122	121	1386	1397	1394	1408	1411	1353
			2	-1	-1	1	-1	1						
28	N K N U	$P2_1/c$	123	122	118	121	123	113	1445	1369	1387	1390	1380	1432
			-1	-3	2	1	-4	4						
			122	120	120	120	125	113	1463	1381	1392	1363	1373	1409
			1	1	-2	-1	3	3						
29	N F S	C2/c	120	119	124	114	123	120	1371	1392	1336	1420	1412	1371
			1	-1	0	1	0	-1						
30	N M S M	$P4_12_12$	124	119	119	121	119	119	1372	1372	1396	1407	1407	1396
			0	-1	1	0	-1	1						
31	N U	$P2_1/n$	121	121	120	118	122	119	1394	1372	1373	1416	1387	1394
			0	0	0	0	0	0						
32	N N N R	$P2_1/n$	123	119	121	119	123	114	1433	1374	1369	1388	1365	1422
			-1	-1	1	1	-3	3						
			122	120	121	119	124	114	1428	1382	1368	1378	1364	1428
			1	2	-2	0	3	3						
33	N U N M B	P-1	123	112	127	115	124	120	1403	1416	1460	1358	1408	1340
			0	0	1	-1	0	1						
34	N X M	$P2_1/c$	122	117	121	122	117	121	1390	1390	1391	1370	1384	1378
			-2	1	1	-2	0	1						
35	N A	$Pbc2_1$	124	118	119	121	121	117	1373	1387	1390	1395	1383	1386
			0	0	0	0	0	0						
36	N M U	$P2_1/c$	124	114	123	122	117	120	1384	1375	1401	1366	1372	1397
			0	0	1	0	0	1						
37	N S	$P2_1/c$	124	118	118	119	124	117	1370	1378	1443	1443	1371	1382
			1	0	-1	1	0	0						
38	N N N Y	$P2_1/c$	122	118	123	116	123	116	1397	1380	1365	1377	1393	1385
			-2	3	-1	-2	3	1						
39	N A	$P2_1/n$	121	120	120	119	121	119	1387	1392	1370	1412	1405	1374
			-1	1	0	0	1	0						
40	N A	$P2_1/a$	121	116	120	126	114	123	1435	1355	1415	1358	1380	1371
			1	-1	0	1	-2	0						
			120	117	122	120	122	119	1441	1421	1398	1389	1365	1372
			0	-1	1	1	-3	2						
41	N N A	$P2_1/c$	122	118	122	118	120	120	1383	1361	1385	1404	1405	1366
			1	0	-1	1	0	-1						
42	N M S M	$P2_1/n$	123	118	122	117	122	118	1393	1394	1381	1410	1403	1377
			1	-2	0	1	-2	0						
43	N A N A N A	P-1	122	118	122	118	122	118	1450	1436	1448	1437	1446	1435
			2	2	0	-3	3	0						

Table 1 (continued)

NO.	Groups	S.G.	α_1	α_2	α_3	α_4	α_5	α_6	d_{61}	d_{12}	d_{23}	d_{34}	d_{45}	d_{56}
			h_1	h_2	h_3	h_4	h_5	h_6						
44	N N N A	$P2_1/c$	124	118	122	119	124	113	1429	1372	1380	1372	1376	1428
			1	1	-2	1	1	2						
45	N A N N N	$P2_1/c$	123	114	122	120	120	120	1367	1428	1434	1361	1384	1377
			2	4	2	1	-3	1						
46	N O A	$P2_1/c$	122	119	120	119	121	119	1372	1380	1390	1407	1387	1385
			-1	0	1	-1	0	1						
47	N A N A N O	$P2_12_12_1$	120	117	122	116	124	119	1414	1442	1435	1437	1420	1373
			6	-4	-2	7	-6	1						
48	N N O B	$P2_12_12_1$	122	117	123	117	122	117	1397	1385	1371	1396	1375	1397
			0	-1	1	1	0	0						
49	N P N T	P-1	126	120	118	119	126	110	1404	1372	1376	1371	1382	1394
			1	1	2	0	2	3						
50	N N O C	$P2_12_12_1$	123	117	123	117	122	118	1382	1376	1370	1406	1402	1370
			0	0	0	0	0	0						
51	N N O	$P2_12_12_1$	123	118	121	119	121	119	1384	1366	1386	1407	1399	1366
			0	0	0	0	0	0						
52	N O N	$P2_1nb$	122	116	122	120	120	120	1392	1399	1400	1382	1389	1357
			0	0	-1	0	1	-1						
53	N N P	$P2_1/n$	122	117	124	117	121	120	1369	1389	1361	1402	1378	1372
			1	0	0	0	1	-1						
			122	118	122	117	121	119	1376	1360	1373	1393	1388	1380
			0	1	0	0	1	0						
54	N P N	P1	123	116	122	120	121	119	1392	1344	1423	1357	1361	1357
			1	-3	3	0	-2	2						
			123	113	126	117	119	121	1346	1401	1382	1349	1411	1363
			2	2	0	3	-3	0						
55	N O P	$P2_1/c$	123	117	122	121	119	118	1420	1398	1377	1383	1398	1384
			0	2	-1	0	1	-1						
56	N O	$P2_1/n$	123	118	120	120	121	117	1371	1376	1385	1378	1380	1385
			0	0	1	0	0	0						
57	N O	$P2_1/a$	122	119	120	120	120	119	1392	1393	1378	1400	1396	1383
			0	0	0	0	0	1						
58	N O C	$P2_1/a$	122	117	122	120	120	119	1358	1401	1373	1373	1392	1392
			0	1	0	0	0	0						
59	N O	$P2_1/a$	121	118	121	122	119	120	1393	1395	1385	1353	1372	1365
			0	0	0	0	0	0						
60	N N N O	$Pca2_1$	122	119	122	118	123	115	1407	1412	1373	1367	1376	1355
			0	0	1	0	0	1						
61	N P	$P2_1/c$	122	118	122	119	120	120	1373	1400	1355	1392	1410	1367
			0	0	0	0	1	1						
62	N M N P T	$P2_1/n$	124	112	126	120	116	122	1368	1386	1392	1382	1403	1393
			2	0	-2	1	0	-2						
63	N N N Q	$Pca2_1$	122	119	122	118	124	116	1384	1389	1369	1378	1360	1388
			-1	1	2	-1	1	2						
64	N N C	Pccn	122	118	122	119	120	119	1391	1385	1388	1399	1394	1387
			1	0	-2	1	0	-1						
65	N B	$Pbn2_1$	125	116	119	124	118	117	1402	1382	1394	1373	1364	1405
			2	-2	2	-2	2	-2						
66	N C C	$I4_1/a$	124	118	119	122	119	118	1371	1355	1385	1377	1366	1389
			0	0	1	-1	-1	0						

Table 1 (continued)

NO.	Groups	S.G.	α_1	α_2	α_3	α_4	α_5	α_6	d_{61}	d_{12}	d_{23}	d_{34}	d_{45}	d_{56}
			h_1	h_2	h_3	h_4	h_5	h_6						
67	N C	$Pna2_1$	123	117	122	119	121	118	1376	1378	1380	1383	1374	1380
			0	0	0	0	0	0						
68	N N C	$P2_1/a$	122	118	123	117	122	118	1402	1376	1386	1388	1372	1392
			0	0	0	0	0	0						
69	N C N C N	Pbcn	122	117	123	117	122	120	1378	1371	1407	1407	1371	1378
			0	0	0	0	0	0						
70	N N C	$P2_12_12_1$	120	121	118	122	119	119	1382	1389	1370	1385	1384	1383
			0	0	0	0	0	0						
71	N C C	$P2_1/c$	123	117	121	120	120	119	1377	1389	1390	1375	1374	1372
			0	1	-1	0	1	-1						
72	N C N C C	$P2_1/c$	121	118	121	120	119	121	1385	1384	1377	1382	1381	1366
			0	0	0	0	-1	0						
73	N N N I	$P4_12_12$	120	120	120	120	120	120	1394	1372	1394	1394	1372	1394
			0	0	0	0	0	0						
74	N C C N C C	C2/m	123	118	118	123	118	118	1381	1381	1392	1381	1381	1392
			0	0	0	0	0	0						
75	N G	$P2_1$	123	118	120	120	121	118	1382	1382	1387	1395	1390	1375
			0	0	1	-1	0	1						
76	N L O	$P2_1/c$	122	118	121	118	121	119	1389	1378	1374	1390	1398	1357
			-1	0	0	0	0	0						
77	N Z	$P2_12_12_1$	123	117	121	121	120	119	1370	1391	1390	1374	1386	1378
			1	2	-1	0	1	0						
78	N J	$P2_1$	123	119	119	121	120	118	1387	1390	1376	1399	1394	1383
			0	1	-1	0	1	-1						
79	N N N K	$P2_1/n$	123	119	122	118	123	116	1390	1369	1361	1372	1368	1392
			1	1	-2	1	1	-2						

* Groups: The substituents positioned at 1-6 with short notation: A NH_2, B Br, C Cl, F F, G CHO, I I, J CN, K CF_3, L $COCH_3$, M CH_3, N NO_2, O OH, P OCH_3, Q OC_2H_5, R $NHNH_2$, S $N(CH_3)_2$, T $C(CH_3)_3$, U $NHCH_3$, V $CONH_2$, W NF_2, X $NHCOCH_3$, Y $N(NO_2)CH_3$, Z N_3 and blank for H atom.

S.G.: Space group.

α_i(in °): The endocyclic angle (the internal angle in benzene ring) at the position i.

h_i(in 0.01Å): The deviation of the i-th C atom from the mean benzene plane.

d_{ij}(in 0.001Å): The bond length between the i-th and j-th C atoms in benzene ring.

	α (°)	h(Å)	d(Å)	α (NO_2)	α (OH)	α (NH_2)	α (CH_3)
ave.	119.98	0.01	1.388	122.80	117.92	116.87	116.85
r.m.s.	3.03	0.01	0.019	1.81	1.61	1.87	2.68
max.	127	0.09	1.436	127	121	119	122
min.	112	0	1.328	120#	115	113	112
χ **				3.49	3.08	2.78	2.63
samples	528	528	528	175	12	21	39

** Group electronegativity, see R.T.Sanderdon,"Polar Covalence", Academic Press, New York(1983)

The minimum α is 118° in hexanitrobenzene.

narity of the benzene ring.

The bond lengths in the ring vary considerably around the average value 1.388 Å, ranging from 1.328Å to 1.463Å, but there seems no simple relation between the above h_i, d_i and the nature of substituent. However, when an intramolecular hydrogen bonding ring is formed, the lengthening of the involved C-C bond (marked with an underline in the table) is measurable due to the repulsion between groups ortho to each other.

A clear distinction can be seen from the statistics on the endocyclic angles (the internal angle in benzene ring). At the position to which a NO_2 group is attached, the α is always greater than 120° , the value for the standard SP^2 hybridization, while the counterpart for amine group, either substituted or unsubstituted, is always less than 120° . The α values for other groups are also consistent with the general trend[1] that the α corresponding to an electron-withdrawing substituent is larger than 120° and the α corresponding to an electron-releasing substituent is less than 120° . The angle has a linear relation[2] with Taft's inductive parameter and Huheey's group electronegativity[9], while the groups at ortho or meta positions have also secondary effect on it. Conversely, the angle could be used to predict related properties[1]. The statistics on the α were listed at the bottom of table 1, showing the linearity approximately (without considering the secondary effect).

CONFORMATION OF NITRO GROUP

Table 2 summerized the main result. Most of symbols in the table could be seen from Fig. 1 with a few exceptions. The Po, denotes the position to which the NO_2 group is attached. When there are more than one molecules in the asymmetric unit, that means, there are conformationally different molecules in the crystal structure, a prime was used to distinquish them.

The d and d' are nearly equal to each other when the NO_2 group is not involved in intramolecular hydrogen bonding. However, when it is involved, the length of the involved N-O bond (underlined) is larger than its conuterpart in the same NO_2 group with almost no exception, due to the repulsion between the groups ortho to each other. The difference is small but significant (up to 0.058 Å).

The γ and γ' are close to each other with a few exceptions. The larger difference than 5° between them were found in 8 out of the 175 NO_2 groups. The sum of $\beta + \gamma + \gamma'$ is always equal to 360° within 1° , although each of them varies in a range of about 20° . It indicates that the NO_2 group and its linked C atom are coplanar or nearly so, though considerable out-of-plane deviation from the ring plane for the whole NO_2 group can occur.

The h_N in table 2 is the distance of the N atom in NO_2 to

Table 2. Conformation of Nitro Group and Packing Properties [§]

No.	Groups	D_x	C_K	△Ho	△Hc	Po	β	γ	γ*	d	d*	h_N	τ	d_{CN}	R_{CN}
1	N M N C	1.799	.768		25.49	1	124	117	119	1223	1205	0	29	1470	
						3	124	118	117	1211	1214	1	80	1471	
2	N M N C M	1.566	.718		28.29	1	128	116	115	1156	1168	5	38	1501	
						3	125	117	118	1212	1185	2	86	1483	
3	N N	1.574	.728	21.0	23.95	1	125	117	118	1244	1197	0	12	1483	
						3	127	117	116	1214	1227	-2	16	1486	
4	N N	1.617	.748	23.0	24.78	1	125	118	118	1220	1218	0	10	1478	
						4	125	118	118	1220	1218	0	10	1478	
5	N M N M N T	1.383	.710		33.22	1	125	117	118	1218	1220	9	80	1479	
						3	123	119	118	1202	1200	7	84	1472	
						5	124	118	117	1220	1228	6	78	1476	
6	N M M M N T	1.265	.707		29.81	1	125	118	117	1213	1222	-7	80	1481	
						5	124	118	117	1224	1218	-5	80	1477	
7	N N M M M M	1.375	.724		30.30	1	124	118	118	1207	1223	0	58	1469	
						2	124	118	118	1215	1215	-1	58	1474	
8	N N N N N N	1.987	.768		31.70	1	125	116	118	1265	1177	0	53	1462	
						2	127	117	116	1236	1222	4	54	1484	
						3	122	119	119	1228	1266	-3	54	1403	
						4	122	119	119	1266	1228	3	54	1403	
						5	127	116	117	1222	1236	-4	54	1484	
						6	125	118	116	1177	1265	0	53	1462	
9	N M	1.284	.691	18.90	20.23	1	123	118	119	1216	1211	-6	3	1477	
10	N	1.378	.715		18.75	1	124	119	117	1216	1199	0	3	1486	
11	N M M M M M	1.221	.724		22.96	1	125	117	118	1184	1181	-1	86	1488	
12	N M N M M M					1	122	119	119	1200	1200	0	90	1480	
						3	121	120	120	1190	1190	0	90	1470	
						1′	123	118	118	1210	1210	0	90	1480	
						3′	123	118	118	1190	1190	0	90	1480	
13	N N N	1.675	.720	25.65	24.65	1	127	118	115	1241	1211	7	3	1493	
						3	125	117	118	1217	1179	-3	29	1475	
						5	125	117	118	1203	1194	-11	7	1470	
						1′	122	120	118	1205	1189	1	6	1442	
						3′	124	118	118	1199	1230	1	9	1480	
						5′	127	116	117	1229	1189	-3	10	1500	
14	N M N N M	1.632	.757	31.02	31.03	1	125	117	117	1212	1212	0	75	1480	
						3	125	118	117	1223	1220	-10	36	1475	
						5	125	117	118	1220	1223	10	36	1475	
15	N N	1.571	.728	20.8	23.80	1	126	117	117	1223	1241	-14	42	1472	
						2	125	118	117	1222	1223	11	42	1470	
16	N N N M	1.653	.741	27.06	28.25	1	124	120	116	1217	1252	5	45	1449	
						3	122	119	119	1195	1215	6	23	1443	
						5	122	119	118	1214	1210	5	52	1496	
						1′	125	116	118	1236	1179	11	42	1494	
						3′	125	119	117	1214	1232	-1	33	1482	
						5′	126	117	116	1177	1232	-8	60	1459	
17	N A N A N V	1.887	.799			1	120	119	121	1228	1233	-29	20	1436	
						3	118	121	120	1234	1241	22	9	1421	1331
						5	122	120	118	1238	1222	30	39	1455	1321
18	N A N A N F	1.944	.810		60.6	1	122	119	119	1229	1230	0	17	1464	1315
						3	118	122	120	1233	1237	-11	5	1433	1319
						5	122	119	119	1230	1217	3	23	1456	

Table 2 (continued)

NO.	Groups	D_K	C_K	△Ho	△Hc	Po	β	γ	γ*	d	d*	h_N	τ	d_{CN}	R_{CN}
19	N U B	1.845	.726			1	116	126	119	1144	1129	-6	4	1438	1362
20	N C A	1.561	.720			1	123	119	118	1235	1235	-7	4	1466	1381
21	N A N	1.627	.753			1	121	119	120	1210	1222	-2	5	1459	1339
						3	121	120	119	1227	1220	-1	9	1452	
22	N A N A N	1.837	.801	34.30	32.67	1	127	118	116	1177	1235	8	5	1514	1323
						3	117	122	121	1262	1242	-4	4	1415	1317
						5	120	119	121	1259	1223	1	5	1433	
23	N S	1.354	.747	24.55	24.70	1	121	120	118	1201	1262	-4	2	1399	1352
24	N X	1.436	.737			1	122	118	120	1218	1229	0	19	1459	1395
25	N N W	1.756	.737			1	124	117	118	1231	1207	3	5	1480	
						3	124	118	118	1211	1232	7	27	1467	1467
						1′	118	123	119	1240	1216	2	22	1473	
						3′	125	117	117	1210	1224	2	36	1483	1461
26	N N N W	1.901	.766			1	126	117	116	1214	1222	-8	62	1493	
						3	126	117	118	1228	1217	6	28	1478	
						5	126	116	117	1223	1225	5	37	1490	1460
27	N M N S	1.442	.739			1	123	118	119	1221	1226	8	19	1453	
						3	124	119	118	1221	1219	-13	66	1468	1360
28	N K N U	1.712	.731			1	121	119	120	1245	1220	-7	6	1434	
						5	126	117	117	1224	1228	-28	50	1455	1322
						1′	121	119	119	1237	1216	2	3	1425	
						5′	124	118	117	1214	1224	23	52	1457	1339
29	N F S	1.451	.741			1	122	118	120	1231	1219	0	3	1437	1344
30	N M S M	1.220	.699			1	123	119	119	1221	1221	0	0	1465	1396
31	N U	1.367	.726			1	122	120	118	1226	1241	4	2	1435	1358
32	N N N R	1.773	.775			1	123	119	119	1233	1226	0	12	1452	
						3	123	119	118	1224	1238	-1	9	1449	
						5	124	118	117	1222	1220	-29	55	1472	1331
						1′	122	118	119	1236	1223	5	1	1449	
						3′	124	118	118	1226	1222	-7	7	1457	
						5′	125	118	117	1218	1222	34	59	1470	1335
33	N U N M B	1.843	.737			1	122	119	119	1209	1197	0	6	1428	1320
						3	126	115	119	1219	1244	-10	73	1480	
34	N X M	1.432	.733			1	124	117	119	1231	1209	-18	44	1460	1410
35	N A	1.435	.734	23.11	17.33	1	122	118	120	1222	1221	1	3	1467	1392
36	N M U	1.320	.722			1	122	120	118	1216	1216	-1	13	1474	1377
37	N S	1.286	.714	22.16	23.53	1	122	119	119	1248	1234	0	10	1492	1404
38	N N N Y	1.730	.744	31.98	31.76	1	125	119	117	1214	1202	-13	25	1485	
						3	126	117	119	1216	1216	-8	25	1488	
						5	127	116	117	1216	1213	18	43	1497	1419
39	N A	1.425	.729	24.09	19.87	1	123	118	119	1227	1229	-2	2	1454	1353
40	N A	1.447	.742	21.05	19.35	1	126	114	120	1216	1223	6	2	1490	1371
						1′	121	118	121	1223	1248	-1	4	1428	1350
41	N N A	1.626	.751			1	126	116	118	1213	1219	4	7	1480	
						3	121	119	120	1225	1250	-5	4	1442	1352
42	N M S M	1.266	.726			1	118	119	123	1225	1203	5	50	1452	1361
43	N A N A N A	1.936	.848	43.6	37.53	1	118	121	121	1236	1243	-8	3	1417	1309
						3	118	121	121	1246	1239	1	3	1417	1319
						5	117	121	121	1243	1260	7	1	1422	1331
44	N N N A	1.772	.768	29.95	28.74	1	124	119	117	1219	1215	6	22	1475	
						3	125	118	118	1224	1222	-3	4	1469	
						5	122	119	119	1202	1230	5	9	1463	1340

Table 2 (continued)

NO.	Groups	D_x	C_K	△Ho	△Hc	Po	β	γ	γ*	d	d*	h_N	τ	d_{CN}	R_{CN}
45	N A N N N	1.859	.767			1	124	118	119	1222	1214	3	2	1461	1312
						3	124	118	117	1217	1218	18	45	1467	
						4	128	116	116	1211	1207	8	65	1486	
						5	124	118	118	1221	1228	-22	19	1447	
46	N O A	1.573	.773		20.67	1	123	118	119	1228	1221	-5	3	1461	1403
47	N A N A N O	1.889	.809			1	118	119	123	1276	1240	18	14	1409	1320
						3	120	120	120	1247	1248	-7	16	1423	1313
						5	124	118	118	1237	1209	22	55	1462	
48	N N O B	2.052	.713		24.60	1	122	119	119	1231	1218	-3	9	1450	
						3	124	118	118	1206	1217	1	5	1477	
49	N P N T	1.357	.713		30.61	1	112	116	132	1225	1193	15	68	1482	
						5	125	118	117	1220	1218	16	63	1490	
50	N N O C	1.754	.730		23.72	1	124	118	118	1210	1219	0	4	1472	
						3	123	119	118	1198	1235	-1	5	1464	
51	N N O	1.667	.750	25.00	23.03	1	124	118	118	1219	1218	-3	5	1484	
						3	123	119	118	1221	1237	-1	3	1449	
52	N O N	1.704	.767	26.79	25.46	1	122	119	118	1215	1242	6	3	1457	
						3	123	119	117	1215	1221	-2	13	1473	
53	N N P	1.552	.728			1	124	117	119	1212	1211	2	8	1467	
						3	124	117	119	1190	1188	3	23	1475	
						1′	124	117	118	1213	1210	3	2	1478	
						3′	123	114	121	1271	1208	1	33	1454	
54	N P N	1.575	.738			1	124	120	115	1201	1229	-2	58	1454	
						3	123	122	116	1188	1210	12	13	1493	
						1′	124	116	120	1214	1208	10	13	1495	
						3′	124	119	118	1200	1221	-2	58	1486	
55	N O P	1.495	.744		24.83	1	121	121	117	1205	1256	0	4	1454	
56	N O	1.476	.728	21.89	16.60	1	123	118	119	1228	1207	-1	1	1474	
57	N O	1.490	.739	23.61	15.73	1	123	119	119	1244	1241	4	7	1450	
58	N O C	1.674	.741		21.59	1	122	119	119	1199	1240	0	1	1442	
59	N O	1.492	.734	17.50	21.43	1	124	119	118	1204	1234	-2	2	1457	
60	N N N O	1.771	.745	25.12	27.20	1	121	120	119	1202	1182	-2	18	1478	
						3	124	118	118	1218	1214	2	1	1455	
						5	122	119	119	1201	1227	-1	7	1456	
						1′	122	121	118	1196	1185	7	20	1464	
						3′	124	118	117	1211	1214	2	6	1466	
						5′	122	120	118	1202	1232	0	2	1449	
61	N P	1.435	.742		21.49	1	122	120	118	1229	1235	0	7	1450	
62	N M N P T	1.303	.698	24.59	29.80	1	123	117	119	1220	1192	4	49	1475	
						3	124	118	118	1211	1199	17	83	1481	
63	N N N Q	1.557	.709	28.80	28.08	1	124	119	117	1205	1234	-8	32	1463	
						3	124	118	118	1222	1216	8	4	1467	
						5	124	118	118	1199	1200	-5	61	1478	
64	N N C	1.799	.768		22.86	1	125	118	117	1224	1225	12	13	1466	
						3	125	117	118	1243	1225	-3	43	1470	
65	N B	1.972	.729		25.31	1	115	123	123	1212	1227	-1	3	1456	
66	N C C	1.683	.704		20.95	1	125	119	116	1198	1228	-4	9	1485	
67	N C	1.576	.721	17.85	20.22	1	124	118	118	1225	1222	-2	3	1481	
68	N N N C	1.772	.717	24.8	25.23	1	125	117	118	1201	1223	3	32	1498	
						3	125	118	117	1225	1227	2	12	1471	
						5	122	118	120	1176	1188	-3	81	1493	

Table 2 (continued)

No.	Groups	D_x	C_K	△Ho	△Hc	Po	β	γ	γ*	d	d*	h_N	τ	d_{CN}	R_{CN}
69	N C N C N	1.932	.741		27.31	1	125	117	118	1217	1224	-5	37	1467	
						3	125	117	117	1206	1206	0	75	1447	
						5	125	118	117	1224	1217	5	37	1467	
70	N N C	1.670	.711		22.87	1	125	117	117	1220	1230	11	38	1470	
						2	125	118	117	1210	1225	-12	46	1481	
71	N C C	1.715	.717		21.07	1	124	117	119	1209	1208	0	53	1471	
72	N C N C C	1.827	.690		24.11	1	126	117	117	1209	1203	1	87	1472	
						3	125	117	118	1212	1200	0	80	1472	
73	N N N I	2.300	.716		29.16	1	132	117	111	1196	1221	0	82	1452	
						3	119	121	121	1167	1167	0	0	1342	
						5	132	111	117	1221	1196	0	82	1452	
74	N C C N C C	1.939	.703		23.25	1	125	118	118	1209	1211	-1	90	1475	
						4	125	118	118	1211	1209	1	90	1475	
75	N G	1.491	.745		21.63	1	122	118	119	1228	1213	-1	2	1460	
76	N L	1.402	.724		23.71	1	123	119	118	1220	1217	-2	4	1466	
77	N Q	1.572	.750		25.18	1	121	119	120	1251	1229	4	5	1447	
78	N J	1.424	.714		21.83	1	124	119	117	1219	1204	-3	10	1483	
79	N N N K	1.939	.703			1	126	116	117	1223	1218	12	50	1479	
						3	127	117	117	1209	1200	-7	15	1490	
						5	126	117	117	1213	1209	8	46	1477	

§ For Groups see table 1. For D_x(g/cm³), Ck, △Ho(kcal/mol), △Hc(kcal/mol) see the last section in text. For β (°), γ (°), γ*(°), d(0.001Å), d*(0.001Å), τ (°) see Fig. 1. For Po, h_N(0.01Å), d_{CN}(0.001Å), R_{CN}(0.001Å) see the third section.

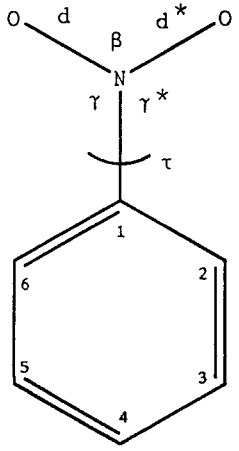

Fig. 1. Conformation of NO_2 Group

Statistics from table 2

	ave.	r.m.s.	max.	min.	samples
| △Ho-△Hc | (kcal/mol)	2.49	2.05	7.88	0.01	26
d_{CN} (0.001Å)	1465	25	1514	1399	175
h_N (0.01Å)	6	6	34	0	175
β (°)	123	3	132	112	175
| γ - γ* | (°)	1	2	16	0	175
| d - d* | (0.001Å)	13	16	88	0	175
R_{CN} (0.001Å)	1361	44	1467	1312	42

the benzene ring plane, representing the out-of-plane deviation of the whole NO_2 group. Large values of h_N up to 0.3 Å were observed when the number of substituents becomes larger and/or the substituent group becomes bigger.

The twist angle τ formed by NO_2 group and benzene ring represents another type of deviation (by rotation). It is also caused by the repulsion, as shown by the data below. The avea-rage values of τ respectively are 8.30° , 29.76° and 56.44° for the cases of No =0, 1 and 2, No being the number of subs-tituents ortho to the NO_2 group. However, intramolecular hyd-rogen bonding formed by NO_2 group and amine or phenolic group greatly reduces the rotation of NO_2 group and thus improves the planarity of the molecule. The corresponding data in this case are 7.08° (No=1) and 18.14° (No=2).

As shown by the statistics appended at the bottom of the table, d_{CN} is signicantly larger than R_{CN}. The d_{CN} is the bond length between the N atom in NO_2 and its attached C atom. The R_{CN} is the counterpart for amine group. According to the above statistics of the α , d_{CN} and R_{CN}, the electron-withdrawing group NO_2 seems push its attached C atom towards the ring cen-ter, making the α and the d_{CN} larger, while the electron-releasing group amine has the opposite behaviour. It is explai-ned by the hyperconjugation of benzene ring with the lone pair of p-type being more effective than SP^2-type[2,3].

SOME PACKING PROPERTIES

Molecular packing analysis was performed on the database by using Gavezzotti's program OPEC[4](Organic Packing and Energy Calculation). Only D_x (in g/cm^3), C_K and PE (in kcal/mol) were listed in this paper. The D_x is the crystal density measured by X-ray diffraction. The Kitaigorodsky's Packing Coefficient[5] C_K is the ratio of the actual volume occupied by the molecules in crystal to the total crystal volume. The molecular volume was calculated by assuming that the molecule consists of spherical atoms having so-called Van Der Waals radii (H 1.20 Å, C 1.70 Å, N 1.55 Å, O 1.52 Å, F 1.47 Å, Cl 1.75 Å, Br 1.85 Å and I 1.98 Å)[6].

The packing energy PE ($-\triangle H_{sub,c}$) was calculated by the atom-atom potential method as usual[5], with the parameters recently revised by Gavezzotti and Filippinni[7]. The PE is the gain of energy when packing 1 mole molecules in gas phase into crystal state, that is, the negative of the sublimation heat ($\triangle H_{sub}$). It is a measure of strength of intermolecular interaction in the crystal, and thus, has important effect on some crystal properties, for example, the vapour pressure, lattice vibration, possible phase transition and thermodynamic properties. For 26 compounds, whose experimental $\triangle H_{sub,o}$ were available[8], the average error for the calculated values, $|\triangle H_{sub,o} - \triangle H_{sub,c}|$ is 2.49 kcal/mol, which is comparable with experi-

mental error, showing that the parameters is generally excellent[7]. However, larger errors were observed, mostly in structures involving intermolecular hydrogen bonding. At present, hydrogen bonding energy was calculated by using same function form(6-exp) with specially derived parameters. In this respect, further improvement in parameters or function form[9] might be desired. Since the experiment measuring $\triangle H_{sub}$ on explosives is not easy and the available data are rare, the calculation method is a very good alternative.

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