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Hypothetical Crystal Structures of Benzene at 0 and 30 kbar

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Abstract

Possible crystal structures of benzene were generated without any prior crystallographic information, using a systematic grid search method. Only structures with one molecule in the asymmetric unit were considered. 31 space groups were investigated, and the resulting structures were clustered and checked for stability upon removal of the space-group symmetry. In the enthalpy range ~10 kJ mol^{-1} 30 structures were found at zero pressure and 20 structures at a pressure of 30 kbar. Their pressure-dependent rankings and interconversions are discussed. The results are compared to previous, less complete, investigations. A possible structure for the high-pressure phase benzene (II), on which only limited powder diffraction data have been published, is suggested.

1. Introduction

The prediction of a crystal structure without the use of experimental information relevant to that particular structure is a great challenge (Gavezzotti, 1994). Benzene is a favorite test case: it is simple to model, a well tested force field is available and the crystal structures of two modifications are experimentally known in detail. All the work reported relies on enthalpy minimization of the starting structures produced by various strategies.

At normal pressure benzene crystallizes in a *Pbca* structure (Bacon *et al.*, 1964) with $Z = 4$ [benzene (I)]. At higher pressures more modifications exist. Thiéry & Léger (1988) discovered benzene (II), which is stable at room temperature between 14 and 40 kbar, and proposed a tentative monoclinic cell on the basis of eight powder diffraction lines. An intermediate phase [benzene (I′)] was suggested from discontinuities in the cell constants of benzene (I). Between 40 and 110 kbar benzene (III) occurs, whose detailed structure ($P2_1/c$, $Z = 2$) has been determined at 25 kbar (Piermarini *et al.*, 1969). In that earlier work, and in much of the literature, this polymorph is identified as benzene (II). We deplore the practice of renaming known modifications, which is bound to lead to confusion sooner or later. However, now that the two notations exist we may just as well adhere to the new one. At higher pressures benzene (III) transforms with apparently minor changes into benzene (III′). Finally, a doubling of the *a* axis appears to occur at 240 kbar [benzene (IV)]. A recent study (Cansell *et al.*, 1993) suggests that this transition involves a chemical transformation and uses the name benzene (IV) for a possible high-temperature phase of benzene (II).

Dzyabchenko (1984*a*) has performed pioneering work on the prediction of benzene structures. Starting from 200 initial models with reasonable intermolecular distances, selected to sample the entire range of possible parameters for special settings in four space groups, he arrived at 17 possible crystal structures. At pressures over 2.2 kbar, benzene (III) was calculated to be more stable than benzene (I) (Dzyabchenko & Bazilevskii, 1985*a*). In a subsequent study Dzyabchenko (1987) allowed two independent molecules in special positions in space group $P2_1/c$ ($Z = 4$). He observed that many previously assumed energy minima were actually saddle points of the potential energy surface when space-group symmetry was relaxed. A search with four independent molecules in space group $P1$ led to 13 energy minimum structures in various space groups (Dzyabchenko, 1989). Six of these structures can be described with one crystallographically independent molecule.

To facilitate our discussion we shall denote the number of crystallographically independent, but chemically identical, molecules in the unit cell by Z''. To our knowledge there is no accepted symbol for this important quantity. The relative multiplicity Z' (Wilson, 1993) does not discriminate between crystal structures with one molecule in the general position ($Z' = Z'' = 1$) and structures with two molecules in different special positions ($Z' \leq 1$, $Z'' = 2$).

Shoda *et al.* (1994, 1995) performed enthalpy minimization on 20 structures taken from a molecular dynamics trajectory, which had been started from an artificial structure with four independent molecules. They recovered the two experimental structures and found two others. A similar procedure was followed by Tajima *et al.* (1995), who performed molecular dynamics calculations on a box containing eight independent molecules. From 40 sampled configurations they obtained 14 possible structures, including the two experimental ones.

Gibson & Scheraga (1995) started from the experimental structure, multiplied the cell axes by various factors and performed energy minimization without symmetry constraints, other than a periodic lattice. From 60 different starts 10 distinct structures were obtained.

Chaka *et al.* (1996) made a more extensive search. They rotated a benzene molecule in increments of 15°, using 2600 starting positions in 13 space groups, and placed it at one certain position in a unit cell, which was constructed by enlarging the van der Waals volume of the molecule by a factor of 2.5. They obtained 14 structures within the energy range 7 kJ mol^{-1}. This is the only work in which a structure with lower energy than the experimental one was reported.

Williams (1996) published a preliminary report of the results of a Monte Carlo procedure which does not assume any space-group symmetry. Starting from four and two independent molecules in the unit cell, the procedure converged to the experimental low- and high-pressure polymorphs, respectively. Leusen (1996) reported similar findings.

Thiéry & Rérat (1996) used a complex force field in an endeavour to identify the high-pressure phase benzene (II). They concluded that a $P2_1/c$ structure, which had also been found by several other workers (Dzyabchenko & Bazilevskii, 1985*a*; Tajima *et al.*, 1995; Gibson & Scheraga, 1995), is the most stable in the pressure range 5–10 kbar. However, agreement between the calculated and observed powder diffraction diagram was poor.

It is very difficult to compare the results of all these studies; only the lattice energies are always reported. Except for the work of Dzyabchenko it is impossible to obtain the atomic coordinates, which are essential to determine whether or not two proposed structures are identical. In the other papers structural details are mostly limited to cell dimensions and an occasional drawing; molecular orientations are not reported. We tried to obtain more detailed information from several authors and they all expressed their willingness to cooperate. However, retrieval of the atomic coordinates turned out to be difficult and in some cases impossible. We suggest that in future work such information should be published or deposited.

The number of possible structures proposed in these studies varies from only a few to ~15 in an energy range of less than 10 kJ mol^{-1}. Based on our experience, we would have expected more. We inferred from the papers cited above that no really exhaustive search has yet been performed in which all relevant parameters were varied systematically. Since our structure prediction program is able to do just that, we applied it to benzene. This paper describes the profusion of structures resulting from that exercise.

2. Searching for possible structures

To produce possible crystal structures for benzene a systematic search was made using the program package *UPACK* (van Eijck *et al.*, 1995; Mooij *et al.*, 1998). A rigid molecule was taken as the asymmetric unit in a given space group and placed with varying positions and orientations in a unit cell with varying dimensions. All triclinic and monoclinic space groups were investigated. Orthorhombic space groups were included only when they occur more than 100 times in the Cambridge Structural Database (January 1996) and have no more than eightfold general positions. Space groups of higher symmetry than orthorhombic cannot (yet) be handled by the program. However, for a symmetric molecule such as benzene quite a few crystal structures may be found that, upon closer analysis, turn out to have more symmetry than the space group in which they were generated.

A rigid benzene molecule was positioned in the x, y plane of a Cartesian axes system, with a C—H bond along the y axis. This molecule was rotated over an angle φ around the z axis, then over θ around the x axis and finally over ψ around the z axis. After this rotation a shift of X, Y, Z was applied; thus, the atomic coordinates are given by

$$\begin{pmatrix} x_n \\ y_n \\ z_n \end{pmatrix} = \mathbf{U}\begin{pmatrix} r\sin n\pi/3 \\ r\cos n\pi/3 \\ 0 \end{pmatrix} + \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}, \qquad (1)$$

where n = 1...6, and the rotation $\mathbf{U}$ is defined by

$$\mathbf{U} = \begin{pmatrix} \cos\varphi\cos\psi - \sin\varphi\cos\theta\sin\psi & \sin\varphi\cos\psi + \cos\varphi\cos\theta\sin\psi & \sin\theta\sin\psi \\ -\cos\varphi\sin\psi - \sin\varphi\cos\theta\cos\psi & -\sin\varphi\sin\psi + \cos\varphi\cos\theta\cos\psi & \sin\theta\cos\psi \\ \sin\theta\sin\varphi & -\sin\theta\cos\varphi & \cos\theta \end{pmatrix}. \qquad (2)$$

D_{6h} molecular symmetry was assumed with radial distances r = 1.397 Å for carbon and r = 2.424 Å for hydrogen (Hall & Williams, 1975).

The rotated and translated molecule was placed in hypothetical crystal structures with **a**, **b** and **c** axes. The crystallographic a axis was chosen to coincide with the Cartesian x axis and the b axis was positioned in the x,y plane, thus keeping the Cartesian components $a_y = a_z = b_z = 0$. Space-group symmetry operations were applied. Owing to the assumed molecular symmetry, φ could be limited to a range of 60°; further details of the search grid are given in Table 1. We only note here that the cell

Table 1. *Settings of the grid search (°, Å)*

	Range	Step
φ	0–60	20
θ	0–90	20
ψ	0–180	20/sinθ
a_x	3.5–20	1
b_y	3.5–20	1
c_z	$V/(a_xb_y)$	—
b_x	0–a_x	1
c_x	0–a_x	1
c_y	0–b_y	1
X	0–a_x/2	1
Y	0–b_y/2	1
Z	0–c_z/2	1

Table 2. *Benzene force fields (kJ mol^{-1}, Å)*

Bond lengths C—C = 1.397, C—H = 1.027 Å

GROMOS (von Gunsteren & Berendsen, 1987) force field, $E = C_{12}r^{-12} - C_6r^{-6}$
United CH atoms, C_6 = 5513, $C_{12} = 1.512 \times 10^7$

Williams & Starr (1977) force field, $E = B\exp(-Cr) - Ar^{-6}$ + Coulomb term

	A	B	C
C—C	2414	367 250	3.60
H—H	136	11 677	3.74
C—H	573	65 485	3.67

Hydrogen charge 0.153 e

volume V, estimated from an approximate density, was used to obtain a starting value for c_z. Of course, in most space groups some angles are fixed by symmetry and it may occur that one or more positional coordinates can be arbitrarily chosen and do not need to be varied.

Since many trial structures were taken, energy calculations have to be fast and a simple force field is needed. Moreover, no combination of exponential repulsion and r^{-6} attraction should be used in this stage, because that leads to a catastrophically large attraction at short distances, which will inevitably occur in trial structures. We used the *GROMOS* force field (van Gunsteren & Berendsen, 1987), which only has a Lennard–Jones 12-6 potential for united CH 'atoms'. Parameters are given in Table 2; a cutoff of 8 Å was used. Of course, such a simple force field should not be used in the final stage of the procedure, but it is good enough to generate a large starting set of hypothetical crystal structures. An important speedup was obtained by stopping a calculation immediately if any atomic repulsion energy term exceeded 10 000 kJ mol^{-1}. This occurred in the majority of cases, so in this way millions of grid points could be eliminated. The remaining structures were subjected to energy minimization, again with several checks where the calculation was stopped unless the energy had dropped below a certain threshold. Only a very limited number of energy minimization cycles were performed before the first list of possible structures was produced. The numbers of entries in this list are given as N_0 in Table 3.

The N_0 list contains many equivalent entries for two reasons: the same structure was usually reached from more than one neighboring grid point and occurred often in different crystallographic settings. It is essential to eliminate such equivalent structures by a fast clustering algorithm (van Eijck & Kroon, 1997) before the time-consuming energy minimization process is continued. The reduction is considerable (N_1 in Table 3). After a longer, but by no means fully convergent, energy minimization (cutoff 10 Å), followed by a second clustering, we arrived at the numbers of structures listed as N_2 in Table 3. This list is short enough to allow the use of a more elaborate force field for further calculations. In common with most earlier studies, we used the exp-6–1 potential of Williams & Starr (1977). Dzyabchenko (1984*b*) has compared this potential with five others and shown that it was the only one that correctly pinpointed the experimental structure. The force field parameters are given in Table 2; convergence acceleration was obtained by Ewald summation for the Coulomb and attractive van der Waals terms.

Table 3. *Results of the search procedure*

Space group	Abundance	N_0	N_1	N_2	N_3
$P1$	0.97	359	61	2	2
$P\bar{1}$	19.32	6344	912	8	4
$P2$	0.03	21	9	1	1
$P2_1$	5.85	821	298	15	5
$C2$	0.86	1668	416	54	24
Pm	0.00	3	2	2	2
Pc	0.38	772	175	24	5
Cm	0.06	35	21	10	6
Cc	1.02	3158	678	67	22
$P2/m$	0.03	2	1	1	1
$P2_1/m$	0.70	49	22	4	3
$C2/m$	0.53	8	3	2	2
$P2/c$	0.51	1262	388	53	13
$P2_1/c$	36.08	11 986	5574	203	45
$C2/c$	7.15	24 372	10 339	291	51
$P2_12_12$	0.50	302	121	24	10
$P2_12_12_1$	9.45	1780	829	33	11
$C222_1$	0.21	688	193	27	11
$Pca2_1$	0.75	571	203	47	12
$Pmn2_1$	0.10	6	4	4	2
$Pna2_1$	1.57	1508	883	88	21
$Cmc2_1$	0.17	19	13	10	4
$Aba2$	0.10	744	252	41	15
$Iba2$	0.08	1081	299	34	6
$Pnna$	0.08	86	43	15	8
$Pccn$	0.37	2056	646	56	15
$Pbcm$	0.15	35	9	4	2
$Pnnm$	0.09	13	5	2	2
$Pbcn$	0.92	1421	597	72	23
$Pbca$	3.93	2345	1132	54	14
$Pnma$	1.61	141	90	18	11
Total	93.57	63 656	24 218	1266	353

The abundance is the percentage occurrence of the space group in the CSD (January 1996). N_0 is the number of structures found in the grid search, N_1 remain after clustering. N_2 is the number of structures after intermediate energy minimization with the *GROMOS* force field, N_3 remain after the calculations with the Williams and Starr potential.

The energy minimization was now continued until forces were less than 0.001 kJ mol^{-1} Å^{-1}, which left 621 structures after clustering. In many cases the benzene molecules were lying in a special position of a space group with higher symmetry than that in which they were generated. To allow clustering of such structures a more robust (but much slower) clustering program was used, which is based only on comparison of interatomic distances. In this way the number of structures was reduced from 621 to 353, listed as N_3 in Table 3.

3. Analysis of the results

As mentioned in the previous section, the symmetry of some resulting structures was higher than that of the space group in which they were initially generated. Consequently, these structures may be encountered in several space groups. After removal of such equivalent structures by the distance-based clustering algorithm, the number of structures was reduced from 353 to 198. Obviously, a comparison of the numbers in Table 3 with the abundance of space groups in the CSD is dangerous; we shall reconsider structural statistics at the end of this section.

Since the generated structures still conform to the symmetry of the original space group, they may correspond to a saddle point of the true energy landscape. To investigate this possibility all structures were treated as if they consisted of independent molecules in space group $P1$ and subjected to further energy minimization. This was performed with full geometry relaxation, assuming a standard intramolecular force field. This relaxation increased the effectiveness of the procedure, but lowered the energy only by a few tenths of a kJ mol^{-1} with respect to structures built from rigid molecules. The space-group symmetry relaxation affected some structures only very slightly, especially those with the lowest energy, but many others changed into an essentially different structure with a considerably lower energy. Indeed, the range of packing energies, which was 23.2–52.2 kJ mol^{-1} for the structures reported in Table 3, was now reduced to 43.6–52.5 kJ mol^{-1}. Out of the 198 structures 73 remained distinct. Based on the interatomic distances, 30 were found to have $Z'' = 1$; the other 43 were more complex. Our search procedure was only designed to find the former type, to which ~90% of the structures belong (Padmaja *et al.*, 1990). Here we have a roundabout way to find a few others for benzene. The highest packing energy encountered for such a structure was 51.0 kJ mol^{-1}, which is 1.5 kJ mol^{-1} less than for the most favorable structure. It is a *Pbcn* structure ($Z = 8$, $Z' = 1$, $Z'' = 2$) with a molecule on an inversion center and another one on a twofold axis.

All structures with $Z'' = 1$ were inspected individually to determine their symmetry properties and to transform them to the actual space group. This was performed with the aid of the program *PLATON* (Spek, 1990), which incorporates the essential procedure *MISSYM* (Le Page, 1988). Detailed results are given in Table 4, where the structures are numbered N1 through N30 (N for normal pressure). The energies reported refer to structures built from rigid molecules; the atomic coordinates can be retrieved using (1).

Some indication of the completeness of the search procedure can be obtained from the structures where the molecules occupy special positions (marked *S* in Table 4). They should have been encountered in every investigated subgroup where the structure can be described with one molecule in the asymmetric unit. The only missing subgroup occurred for structure N13, which was only found in $P2_12_12_1$ and not in $Pca2_1$. It is also of interest to observe that each of the first ten low-energy structures was reached more than once in the $P1$ energy minimization. One structure (N23) was only found in this roundabout way and not directly in space group *Pbca*; here we have obviously reached the energy level where the list of predicted structures may be incomplete. Furthermore, with hindsight we note that the upper limit of 20 Å for cell lengths in the grid search may have been too short for structures with $Z = 8$.

Dunitz (1996) has pointed out that the experimental benzene (I) structure can be altered with not too much deformation into a hypothetical cubic structure in space group $Pa\bar{3}$ ($Z = 4$), defined by $X = Y = Z = 0$, $\theta = 54.74°$, $\psi = 45°$, with a and φ as adjustable parameters. The lowest energy is −51.80 kJ mol^{-1} for $a = 7.88$ Å and $\varphi = 44°$. This elegant structure was not found in our search as it is not in a stable equilibrium, converting into N1.

In our set of 30 structures the space groups *Pbca*, $C2/c$ and $P2_1/c$ predominate. In crystal structure statistics these three groups are fairly frequently encountered (Table 3), but the extreme preponderance of $P2_1/c$ is not reproduced and other popular space groups such as $P\bar{1}$ and $P2_12_12_1$ are found only once in Table 4. Considering the high symmetry of benzene, this is not really surprising. On closer inspection we find that the occurrence of benzene molecules in special positions becomes more rare for decreasing packing energy. In view of the observation of Brock & Dunitz (1994) that centrosymmetric molecules usually occupy inversion centers, we must conclude that, at least in this case, the distribution of hypothetical structures for one molecule is different from the distribution of observed crystal structures in general.

4. Calculations at 30 kbar

As in all earlier work, two experimentally known structures are found: the low-pressure modification (I) as N1; the high-pressure structure (III) as N4 in Table 4. It is not so easy to establish the presence of the high-pressure structures that are only tentatively characterized from their powder diagrams. Since benzene (III′)

Table 4. *Hypothetical benzene structures with $Z'' = 1$*

	E		Z	S	a	b	c	α	β	γ	X	Y	Z	φ	θ	ψ	V/Z
N1	−52.25	$Pbca$	4	$\bar{1}$	6.98	7.43	9.28				0	0	0	12	74	317	120.3
N2	−51.96	$P2_1/c$	2	$\bar{1}$	5.71	6.94	7.20		123		0	0	0	39	117	151	119.5
N3	−51.47	$Pbca$	8		6.92	7.25	19.20				0.01	2.17	7.19	8	99	226	120.4
N4	−51.32	$P2_1/c$	2	$\bar{1}$	5.54	5.57	8.01		108		0	0	0	28	45	316	117.5
N5	−51.14	$P4_32_12$	4	2	5.54	5.54	15.32				0.76	0.76	0	30	135	135	117.5
N6	−50.69	$Pca2_1$	4		9.94	5.42	8.94				1.09	1.50		54	48	136	120.6
N7	−50.01	$C2/c$	8		21.63	5.62	7.85		93		2.61	1.41	2.96	54	144	148	119.0
N8	−49.74	$Pbcn$	4	2	5.62	11.38	7.46				0	2.01	$c/4$	30	32	90	119.3
N9	−49.51	$C2/c$	4	$\bar{1}$	11.74	5.56	7.99		113		$a/4$	$b/4$	0	20	30	185	119.7
N10	−49.27	$Pbca$	8		5.61	8.04	21.39				0.00	3.23	8.07	10	72	327	120.5
N11	−49.09	$Pbca$	8		7.75	12.44	10.11				1.87	4.62	0.83	9	55	71	121.9
N12	−48.85	$P2_12_12_1$	4		5.65	13.22	6.54				0.31	4.96	1.29	24	33	58	122.1
N13	−48.31	$Pbca$	4	$\bar{1}$	5.60	8.19	10.66				0	0	0	51	69	216	122.3
N14	−48.31	$C222_1$	4	2	5.64	11.51	7.46				0	3.50	$c/4$	30	150	270	120.9
N15	−47.68	$C2/c$	8		21.82	5.73	7.89		98		2.48	1.43	1.56	11	140	44	122.0
N16	−46.96	$Pbca$	8		8.41	11.03	10.75				2.54	4.02	0.99	58	65	44	124.7
N17	−46.50	$Pna2_1$	4		7.32	9.93	6.76				1.51	0.66		22	88	52	122.9
N18	−46.47	$P2_1/c$	4		5.41	15.10	6.81		119		1.10	1.92	2.19	35	61	216	121.4
N19	−46.15	$P2_1/c$	4		6.81	7.44	11.88		125		1.70	2.18	0.62	7	51	180	123.5
N20	−46.05	$Pna2_1$	4		10.48	4.97	9.53				3.94	2.06		37	79	50	124.0
N21	−45.79	$C2/c$	8		11.69	5.35	16.35		108		0.91	2.59	1.98	24	147	358	121.7
N22	−45.61	$Pna2_1$	4		5.15	19.22	5.10				0.38	7.32		45	54	133	126.2
N23	−45.57	$Pbca$	8		18.56	10.27	5.26				2.34	0.02	2.39	16	53	309	125.3
N24	−45.49	$R\bar{3}$	3	$\bar{3}$	6.74	6.74	9.36			120	0	0	0	0	0	109	122.6
N25	−45.42	$P2_1/c$	4		5.44	5.45	17.43		105		0.98	1.74	2.23	28	47	136	124.7
N26	−45.27	$C2/c$	8		11.59	5.43	20.03		129		4.92	2.59	1.98	28	148	356	122.6
N27	−44.68	$P2_1/c$	4		5.06	19.66	5.07		97		2.35	2.42	2.32	46	56	226	125.1
N28	−44.59	$P\bar{1}$	2		5.03	5.11	10.17	100	101	98	2.32	2.34	2.41	49	54	131	124.5
N29	−43.81	$C2/c$	8		11.88	12.04	7.42		114		2.21	1.56	2.38	34	133	135	121.1
N30	−43.31	$C2/c$	8		19.08	5.23	11.44		115		1.98	2.56	1.17	21	44	144	128.9

Structures are ordered to their energy E (kJ mol^{-1}). Z denotes the number of molecules in the unit cell; S (if present) denotes a special position. Cell angles not reported are 90°. X, Y and Z are given in orthogonal coordinates (Å); missing entries can be freely chosen. V/Z is the molecular volume in Å^3.

seems to be only a minor modification of benzene (III) (Thiéry & Léger, 1988), we concentrated on benzene (II) and repeated the entire procedure at a pressure of 30 kbar. To this end, enthalpy rather than energy should be considered and so a PV term ($V = a_x b_y c_z/Z$) was added to the energy in all calculations.

We do not report the detailed search results as in Table 3, but only mention the total number of structures: $N_3 = 435$. After elimination of equivalent structures among the various space groups, 261 remained. Upon energy minimization in space group $P1$, this number was reduced to 120; of these 45 had $Z'' = 1$. Due to the effect of the PV term, the enthalpy range is now twice as large as at zero pressure, ~20 kJ mol^{-1}. Therefore, we report only the first 20 high-pressure structures (Table 5, H1–H20), covering the enthalpy range 11 kJ mol^{-1}. Again, these data refer to rigid-body calculations. The effect of allowing flexible molecules is larger than at zero pressure, but still limited to a few kJ mol^{-1}. The experimental high-pressure structure benzene (III) has the lowest enthalpy; this H1 structure corresponds to the low-pressure form N4.

Since the trajectories in enthalpy minimizations may depend on the pressure, one should not expect that the same results can be found by simply starting from low-pressure structures. Indeed, in that way five structures in Table 5 were missed (and no new ones with $Z'' = 1$ were encountered). Four of these transformed to the same structure (N6) upon energy minimization at zero pressure. Where possible, correspondence with the low-pressure structures is indicated in Table 5.

An interesting transition mechanism from N1 to N2 has been proposed by Dzyabchenko & Bazilevskii (1985*a*,*b*). The benzene (I) structure N1 corresponds to H5. However, strictly speaking, this is not an energy minimum: in the high-pressure phase there is a large region with essentially the same energy. One point in this parameter space corresponds to the *Cmca* structure H5*A*, which is unstable and converts to H3 (corresponding to N2). Dzyabchenko and Bazilevskii also discuss the subsequent change from the intermediate H3 to the benzene (III) structure H1 (N4), where the space group remains $P2_1/c$, but the energy barrier is higher. These authors found that the latter structure has the lowest enthalpy at pressures higher than 2.2 kbar. Our energy values are slightly different and we find the transition at 5.5 kbar (see Fig. 1). It is interesting to observe, not unexpectedly, that a small volume at low pressure is an indication that the structure will become more favorable when the pressure is increased.

Table 5. *Hypothetical benzene structures with Z'' = 1 at 30 kbar*

		H		*Z*	*S*	*a*	*b*	*c*	*β*	*X*	*Y*	*Z*	*φ*	*θ*	*ψ*	*V/Z*
H1	N4	141.40	$P2_1/c$	2	$\bar{1}$	5.27	5.33	7.44	107	0	0	0	31	43	225	99.8
H2	N5	141.81	$P4_32_12$	4	2	5.29	5.29	14.29		4.54	4.54	0	30	137	315	100.0
H3	N2	144.39	$P2_1/c$	2	$\bar{1}$	5.42	6.51	6.88	123	0	0	0	21	65	332	101.8
H4	N7	144.70	$C2/c$	8		20.66	5.42	7.22	93	2.48	1.37	2.72	59	30	24	100.9
H5	N1	145.02	$Pbca$	4	$\bar{1}$	6.69	6.75	9.07		0	0	0	6	81	320	102.4
H5*A*	(N2)	145.02	$Cmca$	4	2/*m*	9.12	6.93	6.47		0	0	0	30	142	0	102.2
H6	N8	145.63	$Pbcn$	4	2	5.39	10.90	6.89		0	3.52	*c*/4	30	29	270	101.2
H7	N3	146.10	$I4_1/acd$	8	222	6.67	6.67	18.42		*a*/2	3*b*/4	*c*/8	0	90	225	102.4
H8	N9	146.31	$C2/c$	4	$\bar{1}$	11.16	5.33	7.44	114	*a*/4	*b*/4	0	20	28	185	101.4
H9	N6	146.59	$Pca2_1$	4		9.80	5.04	8.27		1.12	1.38		52	45	141	102.1
H10	(N8)	146.80	$P2_1/c$	4		7.51	5.15	10.95	108	0.60	0.00	3.88	51	69	124	100.7
H11	(N6)	147.41	$P2_1/c$	4		5.60	6.74	11.69	115	2.63	2.14	1.36	47	70	204	100.2
H12	N10	147.42	$Pbca$	8		5.38	7.39	20.48		2.68	2.96	2.52	10	107	31	101.8
H13	N14	148.97	$C222_1$	4	2	5.43	10.98	6.85		0	2.14	*c*/4	30	28	90	102.1
H14	N12	150.72	$P2_12_12_1$	4		5.37	12.38	6.23		2.35	1.55	1.92	26	33	55	103.6
H15	N18	150.74	$P2_1/c$	4		5.25	13.42	6.70	120	2.55	5.03	0.74	36	66	211	102.0
H16	(N6)	150.89	$P2_1/c$	4		5.76	6.70	10.62	93	1.23	0.44	2.60	49	93	202	102.4
H17		151.72	$Pa\bar{3}$	8	3	9.31	9.31	9.31		3.70	3.70	3.70	4	125	225	100.9
H18	N21	151.78	$C2/c$	8		11.11	5.22	15.06	111	2.14	2.52	5.27	24	30	3	102.1
H19	(N6)	152.39	$Pbca$	8		6.91	10.58	11.27		2.98	2.66	1.54	36	114	267	103.0
H20	N29	152.79	$C2/c$	8		11.02	10.98	7.25	112	2.11	1.45	2.40	34	130	136	101.7

H is the enthalpy in kJ mol^{-1}; other entries as in Table 4. The second column gives the corresponding structure from Table 4. Entries within parentheses denote that the H structure converts into the N structure, but not the other way around. Positions and orientations refer generally to different crystal settings than chosen in Table 4. At zero pressure structure H17 converts into a structure with $Z'' = 2$. For a discussion of the metastable structures H5 and H5*A* see text. In space group $I4_1/acd$ the second origin choice (at an inversion center) was taken.

Other investigators (Shoda *et al.*, 1995; Gibson & Scheraga, 1995) have reached the same qualitative conclusion. An exception is the work of Thiéry & Rérat (1996), who (with a different force field) calculated a lower enthalpy for structure H3 (N2) and proposed that this structure should correspond to the experimental benzene (II). However, the correspondence between calculated and observed powder diagrams was poor and these authors suggested that their observations might have been unreliable due to the sluggishness of the phase transitions.

Our work produced a tetragonal structure (H2) which has not been found before, with a relative enthalpy of only 0.4 kJ mol^{-1}. It is shown in Fig. 2. The calculated powder diffraction pattern has a reasonable resemblance to that observed at 31 kbar (Thiéry & Léger, 1988). We also calculated the cell constants at 53 kbar and found a comparable correspondence between calculated and observed interplanar distances at that pressure. The results are shown in Table 6; the r.m.s. deviations were 0.06 and 0.07 Å for the two pressures, respectively. No significant improvement

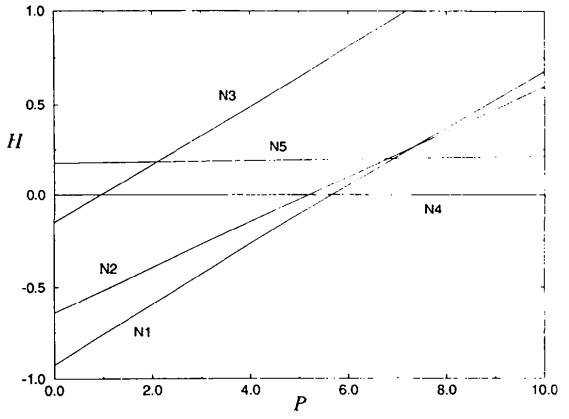

Fig. 1. Enthalpies *H* (kJ mol^{-1}) as a function of pressure *P* (kbar) for the five most favorable benzene structures. The enthalpies are relative to structure N4, which is equivalent to the high-pressure structure H1.

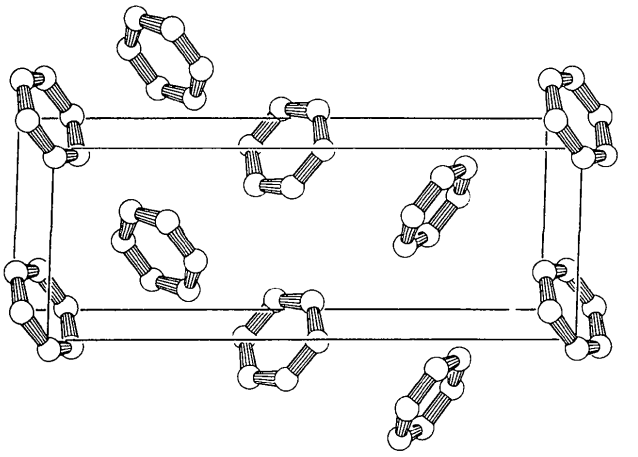

Fig. 2. Structure of the hypothetical structure N5 (H2), which might correspond to the high-pressure form benzene (II). Space group $P4_32_12$, $Z = 4$.

Table 6. *Observed and calculated interplanar distances (Å) in benzene (II)*

		31 kbar			53 kbar		
a (Å)		5.29			5.22		
c (Å)		14.29			13.93		
hkl	I_{calc}	d_{calc}	d_{obs}		d_{calc}	d_{obs}	
101	92	4.961	4.874	m	4.888	4.827	m
102	100	4.252	4.246	vs	4.177	4.200	vs
110	17	3.741	—		3.691	—	
004	34	3.572	3.635	vs	3.483	3.609	vs
103	95	3.540			3.463		
112	25	3.314	—		3.261	—	
104	49	2.961	2.925	w	2.897	2.899	w
113	71	2.942	2.869	w	2.889	2.820	w
114	20	2.584	2.497	w	2.533	2.445	w
210	15	2.366	2.359	w	2.334	2.323	w
211	14	2.334			2.302		
212	10	2.246	2.198	w	2.213	2.160	w

The powder intensities I_{calc} were calculated from structure H2 for Mo radiation, neglecting temperature factors. Calculated lines with relative intensity smaller than 10 are omitted. Observed spacings d_{obs} and visually estimated intensities are from Thiéry & Léger (1988).

Table 7. *Fractional atomic coordinates in hypothetical benzene structures*

	N2, $P2_1/c$, $\beta = 123.11°$			N3, $Pbca$			N5, $P4_32_12$		
	a	b	c	a	b	c	a	b	c
	5.706	6.942	7.203	6.922	7.248	19.199	5.539	5.539	15.321
	x	y	z	x	y	z	x	y	z
C1	0.287	0.000	0.162	−0.001	0.260	0.446	0.336	0.116	0.056
H1	0.498	0.000	0.280	−0.004	0.231	0.499	0.482	0.101	0.096
C2	0.105	−0.109	0.193	−0.123	0.396	0.419	0.158	−0.062	0.056
H2	0.182	−0.189	0.334	−0.214	0.467	0.451	0.173	−0.208	0.096
C3	−0.182	−0.109	0.031	−0.119	0.435	0.348	−0.041	−0.041	0.000
H3	−0.315	−0.189	0.054	−0.208	0.535	0.328	−0.172	−0.172	0.000
C4				0.005	0.338	0.304			
H4				0.008	0.367	0.251			
C5				0.127	0.202	0.331			
H5				0.218	0.131	0.299			
C6				0.123	0.163	0.402	0.315	0.315	0.000
H6				0.212	0.063	0.422	0.446	0.446	0.000

The missing coordinates can be found from the symmetry operation $(-x, -y, -z)$ in the case of N2 and from $(y, x, -z)$ in the case of N5.

could be reached by further adjustment of the cell axes. The correspondence is not nearly as good as for the monoclinic cell proposed by Thiéry & Léger (1988), but that assignment was not constricted by the knowledge of intensities. Moreover, we found no monoclinic structure that could possibly be identified with the published cell constants. We also noted that the proposed indices exclude symmetry elements with a translational component, thus only allowing the space groups Pm, $P2$ or $P2/m$, which are very rarely encountered. We therefore suggest that H2 corresponds to benzene (II).

With regard to the possibly occurring structure (I′), this might well correspond to our structure N3, which can be formed from N1 by doubling the c axis and some rotation of the molecules. The atomic coordinates of the relevant hypothetical structures are given in Table 7.

5. Comparison with earlier work

A comparison of the low-pressure structures with those reported in earlier work is of interest. We have tried to find out which of our structures were already encountered by other investigators; as mentioned in the *Introduction*, this is not easy since complete structural details are difficult or impossible to obtain. One might think that energies calculated with the same force field would be sufficient for a unique identification, but this is not the case: the energies reported for the experimental structure vary by more than 2 kJ mol^{-1} (Table 8). Our energy of −52.25 kJ mol^{-1} compares reasonably well with the value calculated by Williams (−52.39 kJ mol^{-1}, private communication).

Unambiguous comparisons are possible with the structures proposed by Dzyabchenko and Tajima, since

Table 8. *Comparison with published structure predictions ($Z'' = 1$ only)*

	This work	D87	D89	T95	GS95	C96	Experiment
	N1	(I)	(I)	B1, B2	o1	*Pbca**	Benzene (I)
	N2,H3	(II)	(II)	B3	m2	$P2_1/c$	
	N3						Benzene (I') (?)
	N4,H1	(III)	(III)	B4	m1		Benzene (III)
	N5,H2						Benzene (II) (?)
	N6		(V)		o3 (?)		
	N7				m3		
	N8		(*a*)		o2 (?)		
	N9	(IV)	(VI)		m5 (?)		
	N13	(VII)			o4		
	N14		(IX)				
E	−52.25	−52.80	−52.80	−54.54	−52.58	−52.38	

Entries refer to identifications in the following papers: D87: Dzyabchenko (1987); D89: Dzyabchenko (1989); T95: Tajima *et al.* (1995); GS95: Gibson & Scheraga (1995); C96: Chaka *et al.* (1996); (*a*) Dzyabchenko, private communication. *E* is the reported energy (kJ mol^{-1}, Williams and Starr force field) of the first structure.

these authors were so kind in sending us their complete geometries. We shall discuss only structures with $Z'' = 1$ (Table 8). Dzyabchenko (1987) has established that only five of his formerly found structures are stable when no space-group symmetry is enforced. In a later publication (Dzyabchenko, 1989) he introduced two additional structures, but omitted structure N13 which in our energy minimization remained stable. Finally, a structure corresponding to our N8 was found but not published by Dzyabchenko (private communication), thus making a reasonably complete correspondence with our structures that have molecules in special positions.

Tajima *et al.* (1995) have described four of their 14 possible benzene structures in some detail. We repeated the energy minimizations from their coordinates and found that structure B2 changed into B1.

For the other papers we have to resort to guesswork. Gibson & Scheraga (1995) linked four of their structures to the results of Dzyabchenko. These identifications are fairly certain and our structure N7 is also easily recognized. For the other structures the assignments are rather speculative and require changes of space-group symmetry. The data published by Chaka *et al.* (1996) are highly uninformative and it is regrettable that one cannot study their interesting *Pbca* structure, which is claimed to have a lower energy than the experimental structure.

6. Discussion and conclusions

Benzene is a favorable case for structure prediction since a good potential is available. Therefore, one may have more confidence in the calculated energy differences than for more complex molecules, where uncertainty in the force field may preclude reliable predictions.

In the course of this work it became clear that crystal symmetry is frequently lost when it is not enforced during energy minimization. Thus, the procedure followed, where the initial search for crystal structures was carried out for many separate space groups, is unnecessarily laborious. In fact, all structures could have been obtained by searching only the seven space groups $P\bar{1}$, $P2_1$, $P2_1/c$, $C2/c$, $P2_12_12_1$, $Pna2_1$ and *Pbca*. In some previous investigations a number of independent molecules were placed in space group $P1$ and the symmetry of the resulting structures was determined only after the search procedure. Although such a method has not yet given sufficiently complete results, it is potentially more convenient for a molecule like benzene. In that way one can also automatically obtain the structures with more than one molecule in the asymmetric unit. In this work we encountered a few of those in a non-systematic way and although their energy never reaches the lowest value found for the $Z'' = 1$ structures, the difference is sometimes uncomfortably low.

We have tentatively explained the observed benzene (II) powder diffraction lines by the $P4_32_12$ structure H2. The correspondence with the calculated d values is far from perfect, but it is definitely better than for the previously proposed structure H3 (Thiéry & Rérat, 1996). Moreover, according to our calculations structure H2 is only 0.4 kJ mol^{-1} higher in energy than benzene (III), which has the lowest energy for pressures over 5.5 kbar. Such a small difference cannot be significant in view of the limitations of the force field and the neglect of thermal effects. After all, even this good force field is only based on observations under limited experimental conditions, and entropic contributions are neglected altogether. So we suggest that this tentative identification could be useful for further experimental work.

Although the reported structures correspond to minima in the potential energy, it is quite conceivable that some might interconvert when vibrational motion is allowed. This possibility could be investigated by

molecular dynamics simulations, preferably at several pressures. Moreover, in combination with entropy calculations by lattice dynamical methods, such simulations could give an impression of the temperature effect on the relative stability of the various polymorphs. We are considering to undertake that study in the future.

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