References

Burla, M. C., Nunzi, A., Polidori, G., Busetta, B. & Giacovazzo, C. (1980). *Acta Cryst.* A**35**, 573–578.
Cochran, W. & Woolfson, M. M. (1955). *Acta Cryst.* **8**, 1–12.
Giacovazzo, C. (1977). *Acta Cryst.* A**33**, 933–944.
Giacovazzo, C. (1978). *Acta Cryst.* A**34**, 562–574.
Giacovazzo, C. (1980*a*). *Acta Cryst.* A**36**, 362–372.
Giacovazzo, C. (1980*b*). *Acta Cryst.* A**36**, 704–711.
Giacovazzo, C., Spagna, R. Vicković, I. & Viterbo, D. (1979). *Acta Cryst.* A**35**, 401–412.
Hauptman, H. & Kalre, J. (1953). *Solution of the Phase Problem. I. The Centrosymmetric Crystal.* ACA Monograph No. 3. Pittsburgh: Polycrystal Book Service.
Klug, A. (1958). *Acta Cryst.* **11**, 513–543.
Overbeek, A. R. & Schenk, H. (1976). *Proc. K. Ned. Akad. Wet.* **B79**, 341–343.
Weeks, C. M. & Hauptman, H. (1970). *Z. Kristallogr.* **131**, 437–442.

Acta Cryst. (1980). A**36**, 715–723

Calculated Energy and Conformation of Clusters of Benzene Molecules and Their Relationship to Crystalline Benzene

By Donald E. Williams

Department of Chemistry, University of Louisville, Louisville, KY 40208, *USA*

(*Received* 18 *July* 1979; *accepted* 4 *March* 1980)

Abstract

The detailed conformations of benzene clusters containing 2, 3, 5, 7, 9, 11, 13 and 15 molecules were calculated. The nonbonded potential energy of the clusters was minimized by the Newton–Raphson method with exp–6–1 potential functions. All of the clusters exhibited a predominating edge-to-side or herringbone pattern of packing. The concept of intershell coordination, as contrasted to ligand coordination, was introduced and illustrated with the undecamer and larger clusters. The pentadecamer clearly showed the beginning of a second coordination shell. The tridecamer conformation was related to a 13-molecule fragment from crystalline orthorhombic benzene. This crystal fragment has a higher energy than the tridecamer. The fragment can convert to the tridecamer conformation by a process of plane slippage with cooperative molecular motion. Two examples, an isoheptamer and an isotridecamer conformation, are given of clusters with lower total cluster energy but with a higher energy for the reference molecule. In neither case do the conformations follow a smooth trend with increasing cluster size. The isotridecamer has approximate threefold symmetry and has a conformation quite different from the crystal fragment.

Introduction

Molecular complexation or association and subsequent crystallization are caused by the action of weak nonbonded forces between molecules. For hydrocarbons considerable progress has been made in the elucidation of the quantitative nature of these forces in the crystal. The procedure used is to assume a reasonably simple and theoretically justifiable model for the nonbonded potential energy. The coefficients of the nonbonded energy functions are then adjusted to give the best fit to several crystal structures (Williams, 1966; Kitaigorodsky, 1973).

The model for the nonbonded potential energy used here is referred to as exp–6–1:

$$V_{jk} = B\exp(-Cr_{jk}) - Ar_{jk}^{-6} + q_j q_k r_{jk}^{-1}.$$

V_{jk} is a nonbonded pair potential between atoms j and k in different molecules separated by distance r. The first term is the short-range repulsion energy caused by overlap of filled electron shells. The values of C are usually estimated from theory. Values of B for C$\cdots$C, C$\cdots$H and H$\cdots$H interactions are found by fitting observed crystal structures. The second term is the dispersion attraction energy and values for the coefficients A may also be fitted from observed crystal structures. For hydrocarbons, the values of the net atomic charges, q, are small but not negligible. In this study we use the nonbonded parameters of Williams & Starr (1977), set II. These nonbonded parameters are given in Table 1; the geometric mean combining law was used for C$\cdots$H interactions. These parameters give a good fit to the crystal structures of a set of nine aromatic plus nine saturated hydrocarbon crystal structures. It seems reasonable to assume that these

0567-7394/80/040715-09$01.00

nonbonded potential functions are transferable from the crystalline environment to clusters of molecules. A recent review of microcluster structure is available (Hoare, 1979); the studies described in this review were entirely limited to clusters of spherical atoms. We have chosen benzene as an example of the calculation of the detailed cluster conformations for a nonspherical molecule.

Method of calculation

A reference benzene molecule, whose atomic coordinates are given in Table 3, was held fixed at the origin in the *xy* plane. Ligand molecules of identical geometry were introduced around the reference molecule. The orientation of each ligand molecule was specified by a (3 × 3) orthonormal rotation matrix and a translation vector to its center. A center of symmetry was assumed to be present in all clusters except the dimer. For the dimer, the optimum conformation may be found by minimizing the sum of nonbonded pair energies (the total energy of the cluster) with respect to the six degrees of rotational and translational freedom of the second molecule. For the larger clusters, the number of degrees of freedom increases as ligand molecules are added to the cluster. The trimer has the same number of degrees of freedom as the dimer, because of the assumption of a center of symmetry. The maximum number of variables considered was 42 in the pentadecamer cluster. In this cluster there are 15 120 nonbonded pair interactions which must be evaluated during each cycle of energy minimization.

Table 1. *Nonbonded potential parameters* (kJ/mol, Å, e)

Parameter	H···H	H···C	C···C
A	136·	573·	2414·
B	11677·	65485·	367250·
C	3·74	3·67	3·60
q	$q(\mathrm{H}) = 0{\cdot}153$		$q(\mathrm{C}) = -0{\cdot}153$

Table 2. *The minimized cluster energies, reference molecule interaction energies and increments per molecule added to the cluster* (kJ/mol)

No. of molecules in cluster	Cluster energy	Reference molecule energy	Increment per molecule added
2	−11·0	−5·5	−5·5
3	−22·1	−11·0	−5·5
5	−65·7	−21·4	−5·2
7	−108·7	−31·6	−5·1
9	−161·0	−38·5	−3·5
11	−237·6	−44·0	−2·8
13	−305·0	−48·0	−2·0
15	−372·3	−47·6	0·2
7 (iso)	−114·8	−26·8	−2·7
13 (iso)	−325·3	−47·4	−1·7

The cluster energy was minimized by the Newton–Raphson method. All first and second derivatives of the cluster energy were evaluated analytically using a

Table 3. *Rotational orientation matrices and translational vectors defining the optimized cluster conformations*

The Cartesian coordinates of the reference molecule are given, followed by matrices and vectors specifying the position of each molecule in each cluster relative to the reference molecule.

```
MONOMER
 1     1.3970     0.0000     0.0000
 2    -1.3970     0.0000     0.0000
 3     0.6985     1.2098     0.0000
 4    -0.6985    -1.2098     0.0000
 5    -0.6985     1.2098     0.0000
 6     0.6985    -1.2098     0.0000
 7     2.4240     0.0000     0.0000
 8    -2.4240     0.0000     0.0000
 9     1.2120     2.0992     0.0000
10    -1.2120    -2.0992     0.0000
11    -1.2120     2.0992     0.0000
12     1.2120    -2.0992     0.0000
DIMER
a 0.77604-0.44807 0.44384 0.50007 0.86599-0.00011-0.38431 0.22203 0.89611
   3.9144 -0.0002  2.5889
TRIMER
a 0.79447-0.45870 0.39802 0.50001 0.86602 0.00000-0.34470 0.19901 0.91738
   3.8370 -0.0000  2.6724
PENTAMER
a 0.41075-0.45933 0.78759 0.28643 0.88510 0.36682-0.86559 0.07492 0.49512
   4.5971  1.3507  1.2964
b 0.41364-0.27653-0.86743 0.45043 0.89015-0.06898 0.79121-0.36218 0.49275
   1.0728  0.7800  4.7694
HEPTAMER
a 0.66112-0.10816-0.74244-0.32175 0.85308-0.41077 0.67780 0.51045 0.52918
   4.4851  1.2498 -1.5683
b 0.49396-0.07502 0.86624-0.42762 0.84650 0.31715-0.75707-0.52708 0.38606
   0.6457  0.8807 -4.8212
c 0.87338-0.48589 0.03357 0.33955 0.65685 0.67324-0.34917-0.57659 0.73866
   1.4893  4.2093  2.0239
NONAMER
a 0.79960-0.20655-0.56388-0.23364 0.75802-0.60895 0.55322 0.61867 0.55786
   4.9442  1.1879 -1.4451
b 0.57529 0.04853 0.81651-0.40367 0.88505 0.23182-0.71140-0.46296 0.52875
  -0.9061 -1.0604  4.6056
c 0.89990-0.43483-0.03310 0.33538 0.64158 0.68985-0.27873-0.63190 0.72319
   1.5270  4.1618  2.0471
d 0.42880 0.27358 0.86098 0.30694 0.85222-0.42367-0.84966 0.44594 0.28146
  -3.4996  3.4512 -1.0014
UNDECAMER
a 0.93353-0.01556-0.35816-0.12280 0.92475-0.36023 0.33682 0.38027 0.86137
   4.6011  1.6472 -1.9761
b 0.35476-0.34948 0.86718-0.40811 0.77660 0.47993-0.84118-0.52417 0.13288
  -0.0351 -0.6295  4.8854
c 0.92963-0.33321-0.15735 0.28693 0.38662 0.87647-0.23121-0.85994 0.45502
   1.2993  4.5627  1.7135
d 0.29011 0.29277 0.91111 0.23889 0.89976-0.36519-0.92670 0.32360 0.19109
  -3.7733  3.4379 -0.7583
e 0.95175 0.30465 0.03680-0.13222 0.29890 0.94508 0.27692-0.90435 0.32476
   4.6315  0.8345  3.3873
TRIDECAMER
a 0.90970 0.31905-0.26582-0.38885 0.87913-0.27554 0.14578 0.35402 0.92381
   4.6784  2.4932 -2.0401
b 0.19910-0.05311-0.97854-0.51206 0.84574-0.15008 0.83556 0.53095 0.14119
   0.0754  0.3733  4.9459
c 0.98494 0.17291 0.00148-0.06571 0.36637 0.92815 0.15995-0.91426 0.37221
   0.3967  4.9430  0.9821
d 0.99433-0.07372 0.07665 0.08158 0.99111-0.10507-0.06822 0.11073 0.99151
  -3.9916  3.2659 -2.3514
e 0.96394 0.25417-0.07884 0.02244 0.21757 0.97579 0.26517-0.94237 0.20402
   4.6567  1.6798  3.0739
f 0.40941-0.33360-0.84917-0.52964 0.67096-0.51894 0.74288 0.66221 0.09801
  -4.1228  3.3798  2.7270
PENTADECAMER
a 0.93323 0.35039-0.07944-0.34142 0.79602-0.49978-0.11189 0.49353 0.86250
   4.5596  2.4605 -2.5394
b 0.09884-0.08692-0.99130 0.47845 0.87763-0.02925 0.87254-0.47139 0.12833
   0.1554  0.4175  4.9310
c 0.99084 0.12689-0.04625-0.00951 0.40714 0.91332 0.13472-0.90451 0.40462
   0.4470  5.0095  0.8528
d 0.97427-0.13791 0.17829 0.16828 0.97126-0.16830-0.14995 0.19398 0.96948
  -4.0025  3.2022 -2.2801
e 0.80668 0.16524-0.56741 0.54731 0.15334 0.82276 0.22296-0.97426 0.03326
   4.5474  2.4921  2.9331
f 0.41692-0.28285-0.86381-0.55891 0.66967-0.48904 0.71680 0.68669 0.12111
  -3.9474  3.2378  2.8562
g 0.86397 0.14865-0.48110-0.48229 0.51896-0.70575 0.14476 0.84177 0.52006
   7.7838 -0.9357  0.0886
ISOHEPTAMER
a 0.58812-0.32484 0.74067-0.07789 0.88879 0.45165-0.80502-0.32331 0.49741
   4.0936  1.3988  2.1364
b 0.99619 0.08654-0.01094-0.08716 0.98258-0.16413-0.00345 0.16446 0.98638
   3.9477  3.2248 -2.4899
c 0.68085-0.15563 0.71569-0.20561 0.89726 0.39071-0.70297-0.41317 0.57890
  -0.4989 -0.5066  4.6504
ISOTRIDECAMER
a 0.78140 0.58080-0.22824 0.03470 0.32475 0.94516 0.62307-0.74647 0.23360
   1.3819  4.9700  1.0583
b 0.13782 0.31160 0.94016-0.22926 0.93348-0.27578-0.96356-0.17753 0.20009
  -3.6607  3.6559 -0.9840
c 0.72357-0.05885-0.68774-0.62293 0.37350-0.68735 0.29732 0.92576 0.23360
   4.9836  1.3200 -1.1496
d 0.97409-0.21836-0.05888 0.00419 0.27773-0.96065 0.22612 0.93551 0.27145
  -1.9857  2.0836  4.6044
e 0.33362-0.37046 0.86687-0.12849 0.84110 0.43112-0.93391-0.25521 0.25036
  -0.6955 -2.8593  4.5857
f 0.55503 0.22969-0.79908 0.47529 0.70081 0.53193 0.68219-0.67534 0.28023
   2.9417  0.7168  4.5536
```

modified version of the computer program *PCK*6 (Williams, 1979). The rate of convergence to the energy minimum was not fast so that many iterations were necessary. The results for the cluster energies are shown in Table 2. For the dimer, the energy per mole is necessarily exactly one-half of the cluster energy. For the larger clusters, there is no simple relationship between the cluster energies and the energy of the central molecule. The energy of the reference (center) molecule is shown separately, along with the increment of energy obtained by adding molecules to the cluster.

The lowest cluster energy does not necessarily coincide with the lowest energy of the reference molecule. Table 2 shows alternative stable conformations for the heptamer and tridecamer in which higher reference molecule energies were obtained. These were the only such cases encountered, although it is quite possible that other alternative cluster conformations exist. Indeed, the results shown for the clusters may not be the lowest obtainable for the reference molecule energy. In all cases, including the alternative structures, the Hessian of the energy surface was positive definite, indicating that at least a local minimum existed. The regular increments shown in the last column of the table for the normal clusters give a reasonable sequence for optimized reference molecule energies. The isoclusters do not fit into such a regular sequence of cluster energies.

The rotation matrices and translation vectors for the clusters are given in Table 3. Figs. 1–10 illustrate the cluster conformations. Fig. 11 illustrates a thirteen-molecule fragment from the orthorhombic benzene crystal structure.

Description of the calculated cluster conformations

The predicted cluster conformations may be described at various levels of detail. The simplest level is a description of the arrangement of points corresponding to the molecular centers. A more elaborate description is given by including the orientation angles of the ligand molecules. Since the hydrogen atoms are positively charged and the carbon atoms are negatively charged, we expect a tendency toward close C···H approaches because of the Coulombic part of the potential energy. This effect favors an edge-to-side conformation, where the hydrogen atoms at the edge of one molecule are pointed toward the side of the postively charged carbon atoms in the plane of another molecule. Therefore, the dihedral angles between ring planes are often large. This situation is characteristic of the 'herringbone' packing relationship found in crystalline benzene and many other crystals.

The process of building up a cluster of benzene molecules may be described as follows. Figs. 1–8 show projections of the clusters along the *z* axis in the lower halves, and projections along *y* in the upper halves. The reference molecule, *r*, is fixed in the *xy* plane. Table 4 shows the distances and dihedral angles between the reference molecule and the ligand molecules. Table 5 shows a summary of the ligand shifts as the cluster builds up.

In the dimer (Fig. 1), the ring of second molecule, *a*, is partly overlapped with the ring of *r* in the minimum-energy conformation. A C–H group of *r* is oriented across the ring of *a* such that the hydrogen of *r* is almost above the center of a C—C bond of *a*. The

Table 4. *Distances and dihedral angles in the cluster* (Å, °)

Cluster	*a*	*b*	*c*	*d*	*e*	*f*	*g*
Dimer	4·69						
	26						
Trimer	4·68						
	23						
Pentamer	4·96	4·95					
	60	60					
Heptamer	4·91	4·94	4·90				
	58	67	42				
Nonamer	5·29	4·81	4·88	5·02			
	56	58	44	74			
Undecamer	5·27	4·93	5·04	5·16	5·80		
	31	82	63	79	71		
Tridecamer	5·68	4·96	5·06	5·67	5·83	5·99	
	23	82	68	7	78	84	
Pentadecamer	5·77	4·95	5·10	5·61	5·96	5·85	7·84
	30	83	66	14	88	83	59
Isoheptamer	4·82	5·67	4·70				
	60	9	55				
Isotridecamer	5·27	5·27	5·28	5·43	5·45	5·47	
	76	78	76	74	76	74	

intermolecular distance between molecular centers is 4·69 Å and the dihedral angle between ring planes is 26°. The energy of interaction is −5·5 kJ/mol.

Fig. 2 shows that the addition of molecule *a*′, related to *a* by an inversion center at *r*, changes the relationship of *a* to *r* very little. The additional attraction provided by the third molecule decreases the intermolecular distance to 4·68 Å. The molecule translates 0·11 Å, rotates 3°, and the dihedral angle decreases to 23°. The energy of interaction with the reference molecule is −11·0 kJ/mol, essentially doubled from the dimer. The energy of interaction between *a* and *a*′ is slight (−0·1 kJ/mol), but this interaction is still the cause of the small shifts in the intermolecular distances and angles.

Fig. 3 shows the calculated conformation of the pentamer. The new molecules, *b* and *b*′, approach edgewise such that a C–H group is directed approximately toward the ring center of *r*. The dihedral angle is 60° and the intermolecular distance is 4·95 Å. Molecule *a* is strongly affected by the addition of *b*; it moves 2·07 Å around *r* and rotates 40° so that the edge of *r* points approximately towards its face. The dihedral angle of *a* becomes 60° and the intermolecular distance is 4·96 Å. The energy of *r* is −21·4 kJ/mol; the increment of −5·2 kJ/mol per molecule added to the cluster is nearly as great as the first dimer energy. Thus, conformational repulsions have not yet had much effect in restricting the optimum energy orientations of the ligand molecules with respect to the reference molecule. The cluster conformation is approximately square planar. The interaction between *a* and *b* is also optimum. This is shown by the interaction energies of *r* to *a* −5·4, *r* to *b* −5·4 and *a* to *b* −5·3 kJ/mol. The remaining interactions of *a* to *a*′, *b* to *b*′, *a* to *b*′, and *b* to *a*′ contribute only −0·8 kJ/mol to the cluster energy. The total cluster energy is thus 8(−5·4) + 24(−5·3) − (0·8), which is −65·7 kJ/mol when the numbers are properly rounded.

In the heptamer (Fig. 4) molecules *c* and *c*′ approach to complete an approximate octahedral coordination about *r*. The new molecules are 4·90 Å from *r* and have dihedral angles of 42°. To accommodate the new molecules, molecules *a* and *a*′ move around the edge of *r* by 2·87 Å and rotate by 67° to arrive at a dihedral angle of 58°. Molecules *b* and *b*′ move 2·39 Å and rotate 55° to arrive at a dihedral angle of 67°. The energy of *r* in the cluster is now −31·6 kJ/mol, for an increment of −5·1 kJ/mol per molecule added. Thus, there is still sufficient space about *r* to allow a nearly optimum interaction with six surrounding molecules in the heptamer. The individual interaction energies are *r* to *a* −5·2, *r* to *b* −5·2, *r* to *c* −5·3 kJ/mol. Molecule *c*, however, does not achieve maximum interaction with *a* and *b*, although *a* continues to interact optimally with *b*. The individual energies are *a* to *b* −5·3, *a* to *c* −2·4, *b* to *c* −2·8 kJ/mol.

After we reach the nonamer (Fig. 5) the positions of *a* and *b* become more stable. Molecule *d* approaches the largest face of the octahedron of the heptamer, which may be seen in the lower half of Fig. 4. The resulting configuration is approximately square prismatic; in the upper half of the figure two planes containing four molecules each may be discerned. Molecule *d* is 5·02 Å from *r* and its dihedral angle is 74°; an edge of *r* is directed toward the plane of *d*. To

Table 5. *Summary of the rotational and translational shifts as the cluster size increases*

The three entries are the translation of the molecular center, the rotation of the molecule and the dihedral angle change.

Cluster sizes		Shifts for molecule					
from	to	*a*	*b*	*c*	*d*	*e*	*f*
2	3	0·11 3 3					
3	5	2·07 40 40					
5	7	2·87 67 62	2·39 55 54				
7	9	0·48 15 15	0·38 10 10	0·06 5 4			
9	11	0·78 26 26	1·01 28 27	0·57 21 20	0·37 10 7		
11	13	0·85 20 8	1·01 26 26	1·22 31 11	1·62 73 73	0·90 10 10	
13	15	0·51 18 17	0·09 7 7	0·15 4 3	0·10 8 7	0·83 32 31	0·26 3 2

accommodate the addition of *d*, molecule *a* moves 0·48 Å and rotates 15° to arrive at a dihedral angle of 56°. Molecule *b* moves 0·38 Å and rotates 10° to arrive at a dihedral angle of 58°. Molecule *c* moves 0·06 Å and rotates 5°, to attain a dihedral angle of 44°. Thus, the motion of molecules *a*, *b* and *c* is not too large, showing the onset of somewhat greater rigidity for the nonamer. The energy of *r* is now −38·5 kJ/mol, for an increment of −3·5 kJ/mol per molecule added. The smaller increment indicates that the interactions of *r* with the ligands are no longer completely optimum because of space requirements in the coordination shell. In the nonamer the *r* to *b* and *r* to *c* energies are still −5·1 kJ/mol; but the *r* to *d* energy drops to −4·7 and the *r* to *a* energy drops to −4·3 kJ/mol. The only optimum interaction between ligand molecules is the *a* to *b* energy of −5·2 kJ/mol. The next largest interligand interaction energies are −3·6 kJ/mol or weaker.

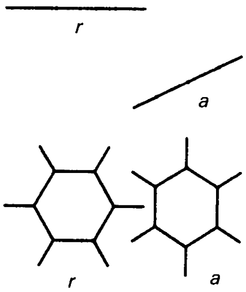

Fig. 1. Dimer. The lower half shows a projection along *z*. The upper half shows a projection along *y*.

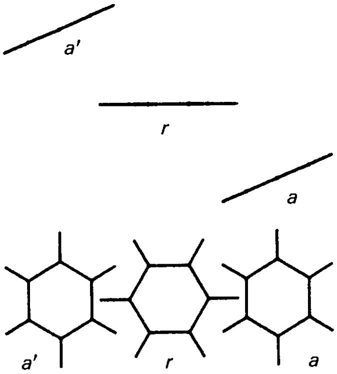

Fig. 2. Trimer.

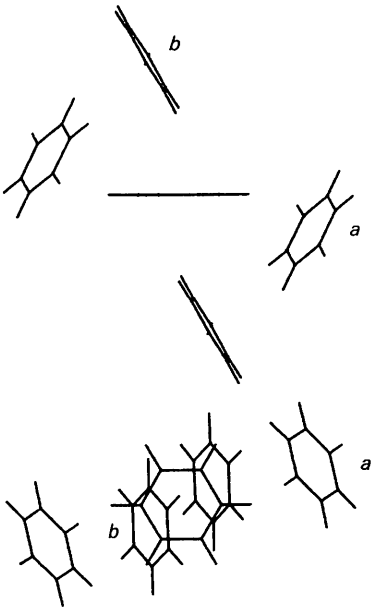

Fig. 3. Pentamer.

In the undecamer (Fig. 6), molecule *e* positions itself to obtain good interaction with *b*′, *c* and *d*. The interaction of *e* with *r* is not as good, being an edge-to-edge orientation with nearest contacts between positively charged hydrogens. The weaker interaction with *r* is reflected in the increased *e*–*r* distance of 5·80 Å; the dihedral angle is 71°. Molecule *a* (and *a*′) moves 0·78 Å and rotates 26° to a new dihedral angle of 31°. Molecule *b* moves 1·01 Å and rotates 28° to a new dihedral angle of 82°. Molecule *c* moves 0·57 Å and rotates 21° to a dihedral angle of 63°. Molecule *d* moves 0·37 Å and rotates 10° to a dihedral angle of 79°. The energy of *r* becomes −44·0 kJ/mol, for an increment of

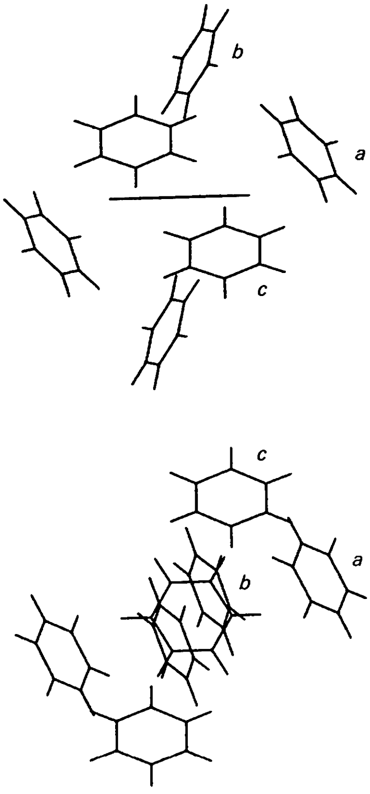

Fig. 4. Heptamer.

only −2·8 kJ/mol for each of the added molecules. The interaction of e and e' with r is thus not optimum; the energy of interaction is −3·0 kJ/mol. It is perhaps too early to designate e as a member of the second coordination shell, but e interacts more strongly with b', c and d than with r.

The energies of interaction are e to b' −4·8, e to c −4·7, e to d −5·1 kJ/mol. All these interactions are stronger than the interaction of e to r. Even the e to a interaction energy of −3·8 kJ/mol is larger than the e to r energy. If we refer to r as ligand-coordinated, e can be described as shell-coordinated with the other ligand molecules. As a result of their coordination with e, the b, c and d molecules show a slightly decreased interaction with r: the energies are r to b −5·0, r to c −4·6 and r to d −4·6 kJ/mol. The r to a interaction actually increases from −4·3 in the nonamer to −4·8 kJ/mol in the undecamer. The next largest interaction is the familiar a to b one of −3·9 kJ/mol. All others are −2·9 kJ/mol or weaker. The overall conformation, as viewed in the lower half of Fig. 6, is of the 2:6:2 type with a nearly planar ring of six ligands (a, a', b, b', e and e') around r.

In the tridecamer (Fig. 7), molecule f strongly affects the position of d, compared to its position in the undecamer. Molecule f does not coordinate closely with r; the energy of interaction is only −2·7 kJ/mol. The r–f distance of 5·99 Å also indicates loose coordination. Molecule f is shell-coordinated with c' and d; the energies of interaction are −5·1 kJ/mol each. The interaction of f with b (−3·8 kJ/mol) is also stronger than that of f with r. The geometrical relationship of f to c' and d is edge-to-side, similar to the relationship of b to r (see the lower half of Fig. 7). The c'–f and d–f distances of 5·09 and 5·08 Å also indicate a strong interaction. Molecule d moves 1·62 Å, rotates 73°, and acquires a new dihedral angle of only 7° with r.

As for the other molecules, a moves 0·85 Å and rotates 20° to a new dihedral angle of 23° and an interaction energy of −4·1 kJ/mol with r. Molecule b moves 1·01 Å and rotates 26° to a new dihedral angle of 82°; the interaction energy with r is −5·1 kJ/mol. Molecule c moves 1·22 Å, rotates 31° to a dihedral angle of 68°, with an interaction energy of −5·2 kJ/mol. Molecule e moves 0·90 Å, rotates 10° to a dihedral angle of 78°, with an interaction energy of −2·8 kJ/mol.

Molecule e is shell-coordinated with a, b' and d; the interaction energies are −5·0, −4·8 and −5·2 kJ/mol. In the undecamer, molecule e was shell-coordinated with b', c and d. The shift in the position of e takes it toward a; also note in the top halves of Figs. 6 and 7 that c moves to the left, away from e.

The energy of r becomes −48·0 kJ/mol, which

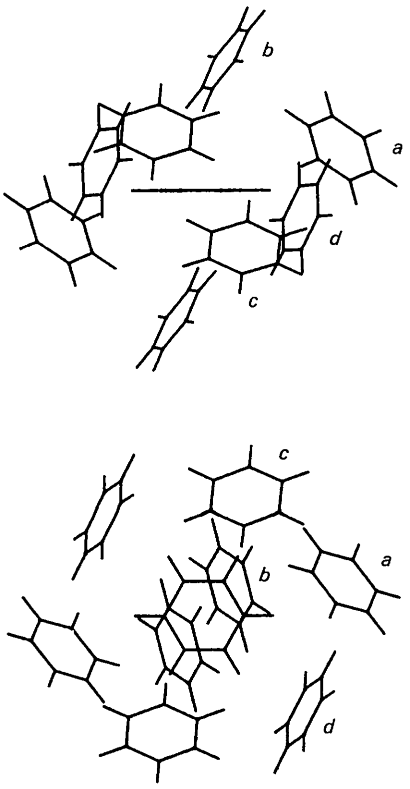

Fig. 5. Nonamer.

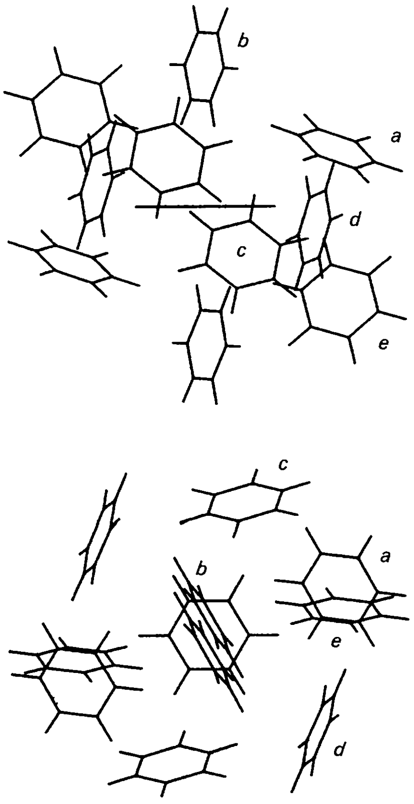

Fig. 6. Undecamer.

shows an increment of only −2·0 kJ/mol each for the two added molecules. As discussed above, most of the energy of interaction of *f* and *f*′ is of the shell-coordination type.

The overall conformation of the tridecamer, as seen in the lower half of Fig. 7, is of the 3 : 6 : 3 coordination type. The interligand angles show considerable scatter, but the values are closer to cubic closest packing than to dodecahedral. Note that hexagonal closest packing is prohibited by the inversion symmetry.

In the pentadecamer (Fig. 8), molecule *g* clearly initiates the second coordination shell. The interaction energy of *g* with *r* is only −0·6 kJ/mol and its distance from *r* is 7·84 Å. The coordination of *g* is to the outside of the ligands forming the first shell, especially to *a*, *d*, *e* and *f*. The respective energies of interaction are −4·5, −4·8, −3·7 and −4·5 kJ/mol. The addition of *g* (and *g*′) disturbs the coordination about *r* so that the interaction energy of *r* with all surrounding molecules, including *g*, is decreased to −95·4 kJ/mol. Thus, the coordination about *r* is deoptimized in order to get a better coordination of *g* with the outside of the molecules in the first coordination shell. Table 5 shows that overall the first-shell molecules *a* to *f* only move small amounts to accommodate *g*. The largest movement is that of *e*, which translates 0·83 Å and rotates 32°.

The isocluster conformations

The isocluster conformations were recognized by examination of the increments per molecule added to the cluster (Table 2). The isocluster increments are anomalous and do not fit into the pattern of the other increments. It is possible that other isoclusters exist which were not located. The regular increments shown by the normal clusters are consistent with the view that the coordination energy of *r* should increase in a uniform manner.

Fig. 9 shows an alternate conformation of the heptamer. This isoheptamer cluster has an energy of −114·8, which is lower than the energy of −108·7 kJ/mol for the heptamer cluster discussed above. However, the energy of *r* in the isoheptamer is −26·8, which is less than the energy of *r* in the heptamer, −31·6 kJ/mol. Since our main concern is with the optimum coordination about *r*, we treat such isoclusters separately.

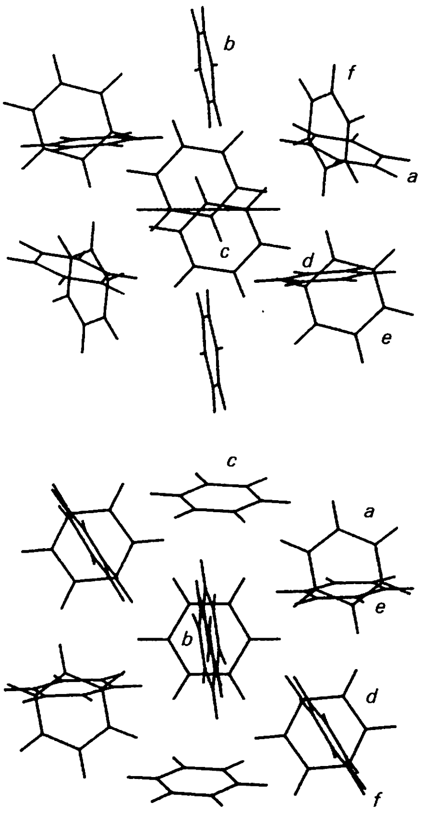

Fig. 7. Tridecamer.

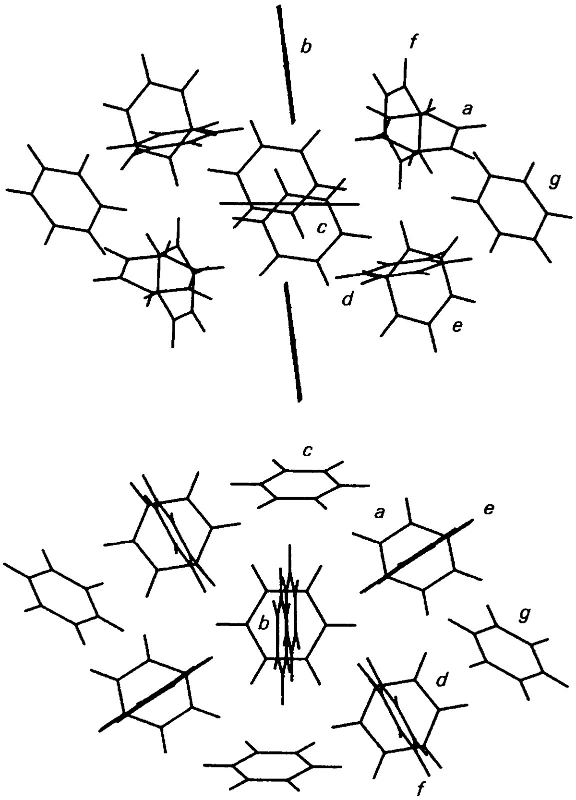

Fig. 8. Pentadecamer.

The conformation of the isoheptamer is a hexagonal disc. The six ligand molecules encircle *r* so that all of the interligand energies of interaction are better than in the normal heptamer. The three pairs of interligand energies are −5·4, −5·0 and −4·4 kJ/mol. In the normal heptamer, the three pairs of greatest interligand interaction are −5·3, −2·8 and −2·4 kJ/mol, which are substantially less. In the isoheptamer, the energies of interaction with *r* are −4·8, −4·6 and −4·1 kJ/mol. These are slightly less than the corresponding values of −5·3, −5·2 and −5·2 kJ/mol in the normal heptamer. Thus, it is seen that the most essential difference between the isoheptamer and the normal heptamer is that a considerable increase in interligand interaction energy is obtained while only a slight sacrifice is made in the reference molecule interactions.

Fig. 10 shows an alternate conformation of the tridecamer. This isotridecamer cluster has an energy of −325·3, which is lower than the energy of −305·0 kJ/mol for the tridecamer cluster discussed above. However, the energy of *r* in the isotridecamer is −47·4, which again is less than the energy of *r* in the tridecamer, −48·0 kJ/mol.

The conformation of the isotridecamer is similar to cubic closest packing. There exists an approximate threefold axis of symmetry (Fig. 10). The benzene ring is encircled by six ligand molecules, with triads of ligands above and below. As with the isoheptamer, the loss of interaction energy with the reference molecule is more than offset by the gains in interligand interaction energy. The interligand relationships show the favorable edge–side conformations.

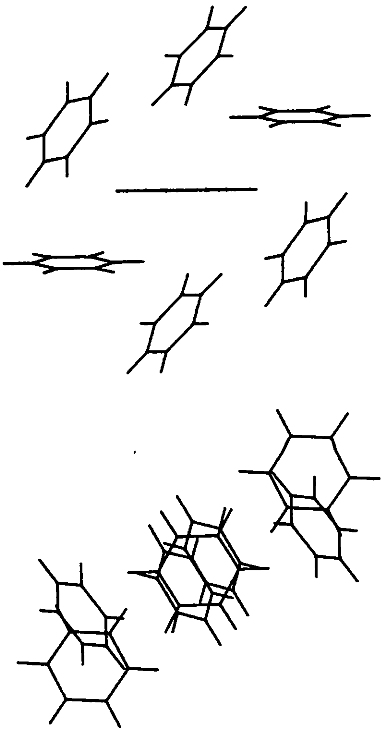

Fig. 9. Isoheptamer.

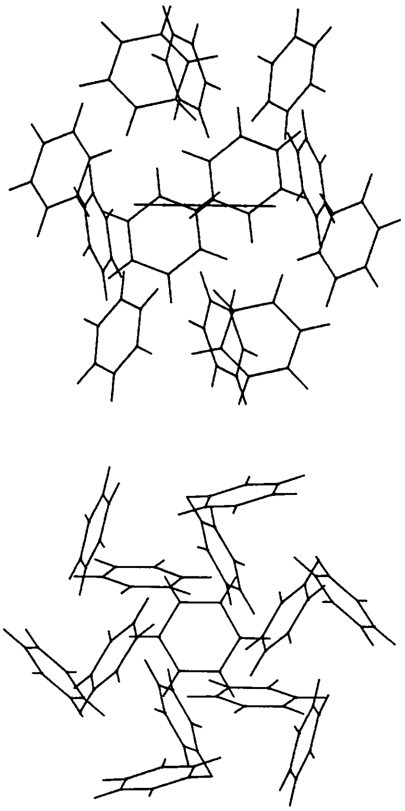

Fig. 10. Isotridecamer.

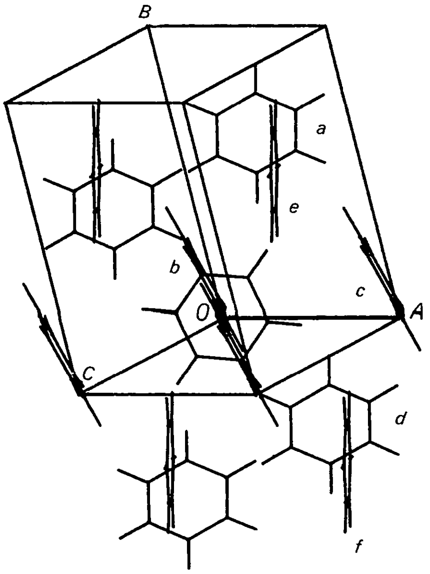

Fig. 11. Tridecamer fragment from orthorhombic benzene. The outline of the unit cell is shown.

We view the isoclusters as competing species not along a smooth route to large cluster formation. Under the agitation of thermal motion, the isoclusters could break up and reform the normal cluster which could lead to crystallite formation.

Relationship of the tridecamer cluster to crystalline benzene

The normal crystalline form of benzene is orthorhombic, space group *Pbca*, with four molecules per cell (Bacon, Curry, & Wilson, 1964). The molecules lie on inversion centres, each with an identical packing environment. The inversion centers are located at the face centers of the cell. Thus, the arrangement of the molecular centers would be face-centered cubic if all lattice constants were equal. The actual lattice constants are $a = 7{\cdot}39$, $b = 9{\cdot}42$ and $c = 6{\cdot}81$ Å at a temperature of 138 K. The four molecules located at positions of the type $(\frac{1}{2},0,\frac{1}{2})$ are closest, at a distance of 5·02 Å. They have an edge-to-side relationship with the reference molecule (Fig. 11), with a dihedral angle of 87° and a calculated interaction energy of −4·8 kJ/mol. These values may be compared to a distance of 4·96 Å, a dihedral angle of 82° and an energy of −5·1 kJ/mol for *b* in the tridecamer cluster.

The second closest molecules in orthorhombic benzene are located at $(0,\frac{1}{2},\frac{1}{2})$, at a distance of 5·81 Å. The dihedral angle is only 29° and the energy of interaction is −3·4 kJ/mol. These values may be compared to a distance of 5·67 Å, a dihedral angle of 7°, and an energy of −4·1 kJ/mol for *d* in the tridecamer.

The third closest molecules in orthorhombic benzene are located at $(\frac{1}{2},\frac{1}{2},0)$ at a distance of 5·99 Å. The dihedral angle is 86° and the energy of interaction is −2·4 kJ/mol. These values may be compared to a distance of 5·99 Å, a dihedral angle of 84°, and an energy of −2·8 kJ/mol for *e* in the tridecamer.

The relation between the tridecamer cluster and the crystal may be viewed as a slippage of planes, which can be seen in the lower half of Fig. 11. The reference plane contains molecules *r*, *b*, *d* and *f*. The plane containing *c*, *a* and *e* can slip from the upper left toward the lower right. This brings *a* and *e* into rough correspondence with Fig. 7. In this process fairly large shifts occur for *b* and *e* of the crystal fragment.

The energy barrier for this type of plane slippage, with cooperative motion of the molecules, should not be large. In this way the crystal fragment can be transformed into the tridecamer cluster. We visualize the plane slippage process occurring simultaneously with the addition of more molecules to the cluster.

The crystal fragment shown in Fig. 11 has a reference molecule energy of −42·7, compared to the tridecamer cluster energy of −48·0 kJ/mol. It is expected that the cluster would have a lower reference molecule energy than the crystal fragment, since the ligand orientations in the cluster are not restricted by the long-range-order requirement of a lattice. The crystal fragments, of course, may be joined together perfectly to form the crystal where the reference molecule energy is −52·3 kJ/mol. This value is the observed heat of sublimation of benzene, corrected for zero point energy (Williams, 1974). For the same reason, the total tridecamer cluster energy, −376·6, is lower than the crystal fragment energy of −279·0 kJ/mol.

This research was supported by National Institutes of Health grant number GM16260.

References

BACON, G. E., CURRY, N. A. & WILSON, S. A. (1964). *Proc. R. Soc. London Ser. A*, **279**, 98–110.
HOARE, M. R. (1979). *Adv. Chem. Phys.* **40**, 49–136.
KITAIGORODSKY, A. I. (1973). *Molecular Crystals and Molecules*. New York: Academic Press.
WILLIAMS, D. E. (1966). *J. Chem. Phys.* **45**, 3770–3778.
WILLIAMS, D. E. (1974). *Acta Cryst.* A**30**, 71–77.
WILLIAMS, D. E. (1979). *Quantum Chemistry Program Exchange*, **11**, 373.
WILLIAMS, D. E. & STARR, T. L. (1977). *Comput. Chem.* **1**, 173–177.