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Selective Clathration of Hydrocarbons by 4-*p*-Hydroxyphenyl-2,2,4-trimethylchroman (Dianin's Compound)

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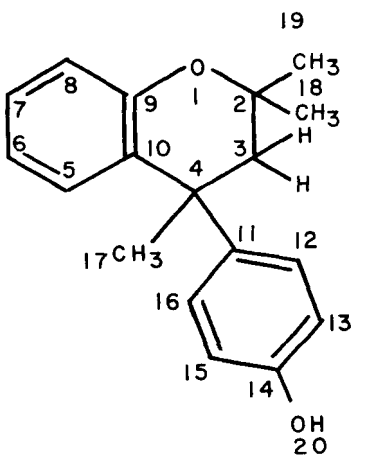
Summary

Dianin's compound has been found to exhibit a marked selectivity when clathration occurs from mixtures of hydrocarbons in the C_5–C_{10} range. X-ray investigations of clathrates formed from single hydrocarbons show that unit cell dimensions vary only slightly according to the guest component and that small changes in intensity of the diffraction patterns occur. Both the mole ratio (Dianin's compound:guest) and selectivity (composition of hydrocarbon component of clathrate) depend upon the rate of crystallization of Dianin's compound from solution. Under comparable conditions of crystallization, studies with binary blends have shown that the ratio of components in the guest is proportional to the ratio of components in the solution from which clathration occurred. The ease of clathration of a component in Dianin's compound relative to a reference component is termed the relative accommodation factor. Using *n*-heptane as the reference hydrocarbon and crystallizing Dianin's compound from equiweight multicomponent mixtures containing *n*-heptane, relative accommodation factors for many C_5–C_8 paraffins, a few naphthenes and olefins, and a number of C_6–C_{10} aromatic hydrocarbons have been obtained. With paraffin hydrocarbons selectivities are in accord with those expected from the known dimensions of the cage. Aromatic hydrocarbon selectivities, however, follow a more complicated pattern, and it is possible that with less flexible structures of this kind "trapping" during the formation of the cage plays a more dominant role. Various applications of Dianin's compound are

discussed, and it is suggested that the basic structure should be sufficiently stable to allow some modification so enabling "tailor-made" host compounds to be synthesized for specific separations.

Since Powell first established the true nature of the quinol complexes as cage compounds or clathrates, considerable interest has been shown in this unique class of molecular compounds (*1*, *2*). Most fundamental investigations (*3–6*) have concentrated on the quinol clathrates and gas hydrates, and this has led to a better understanding of the thermodynamic aspects of complex formation. Molecular compounds are not only of interest from the physicochemical point of view but have also excited interest as selective agents capable of effecting separations difficult or impossible by conventional methods (*2*, *7*, *8*). Rather surprisingly, Dianin's compound (4-*p*-hydroxyphenyl-2,2,4-trimethylchroman I), discovered in 1914 (*10*) and reinvestigated by Baker et al. (*11*, *12*) and



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Powell et al. (*13*) over a decade ago, appears to have been largely neglected from both points of view. Because of the large dimensions of the cage (*13*) and the known ability of Dianin's compound to form clathrates with hydrocarbons, we decided to investigate the selectivity that occurred when Dianin's compound was crystallized from hydrocarbon mixtures.

EXPERIMENTAL

Dianin's compound was prepared by the method described by Baker et al. (*12*). The product was recovered as the ethanol clathrate and isolated in the "guest-free" form by sublimation at 140–150°C at 0.1 mmHg pressure (mp 157–157.5°C).

Clathrates of aromatic hydrocarbons were prepared by dissolving Dianin's compound at just below the atmospheric boiling point of the solvent and allowing the solution to cool. With paraffins and naphthenes this simple procedure was unsatisfactory because of the low solubility of Dianin's compound in these hydrocarbons. In initial investigations we therefore adopted a Soxhlet extraction procedure similar to that used by Baker et al. (*12*) in their preparation of the methyl iodide clathrate. This procedure, however, requires appreciable quantities of hydrocarbon and since we wished to examine clathrates formed from a wide range of different blends, we developed a sealed-tube technique enabling selectivity studies to be made on as little as a 100 μl of hydrocarbon. In a typical investigation a few crystals of Dianin's compound (ca. 100 mg) and hydrocarbon solvent (ca. 250 μl) would be weighed into a thick-walled

TABLE 1

Mole Ratios of Clathrates Prepared from Pure Hydrocarbons

Hydrocarbon	Mole ratio, Dianin's compound:hydrocarbon
n-Hexane	5.9
n-Heptane	6.0 ± 0.3
3-Methylhexane	5.9 ± 0.4
2,2-Dimethylpentane	6.6 ± 0.4
n-Octane	7.5
2,2,4-Trimethylpentane	8.1 ± 0.7
n-Nonane	17.3
n-Decane	106
Cyclopentane	5.8
Cyclohexane	6.9
Benzene	6.3
Toluene	6.5
Ethylbenzene	6.3
o-Xylene	12.6
m-Xylene	6.5
p-Xylene	6.6

TABLE 2

Single Crystal X-Ray Data[a]

Clathrate	a(Å), hexagonal	c(Å), hexagonal	V(Å^3), hexagonal	a(Å), rhombohedral	α	Density (g/cc)	Mole ratio
Pure	26.99(1)	10.96(3)	6915	16.01	114°57′	1.165(6)	
Ethanol	26.95(2)	10.99(2)	6908	15.98	114°54′	1.225(6)	3.0
n-Heptane	27.11(1)	10.96(1)	6976	16.08	115°00′	1.204(6)	7.5
2-Methylhexane	27.22(1)	10.94(1)	7020	16.13	115°02′	1.218(4)	5.5
3-Methylhexane	27.32(4)	10.89(1)	7042	16.19	115°06′	1.207(6)	6.0
2-Methylheptane	27.18(1)	10.94(2)	6996	16.11	115°02′	1.216(4)	6.5
Benzene	27.25(2)	10.94(2)	7035	16.15	115°04′	1.197(4)	6.3
o-Xylene[b]	27.03(2)	10.95(3)	6929	16.03	114°58′	1.170(6)	30
m-Xylene[b]	27.13(4)	10.93(2)	6969	16.08	115°02′	1.206(6)	7.5
1,3,5-Trimethylbenzene[b]	27.20(5)	10.75(3)	6888	16.11	115°12′	1.18(1)	42
Methyl iodide	27.07(4)	10.96(2)	6957	16.05	114°58′	1.370(6)	2.7

[a] Estimated errors shown in brackets refer to last decimal place.

[b] See text footnote, p. 795.

Pyrex glass capillary tube closed at one end. This was then cooled in liquid nitrogen, evacuated, and sealed at the other end. The sealed tube was then totally immersed in an oil bath and the temperature raised until the Dianin's compound dissolved (generally around 140–150°C). On cooling, the clathrate precipitated and was easily recovered by breaking open the capillary, pipetting off the supernatant liquid, and drying the crystals under a gentle stream of air. A difficulty with this procedure was that the Dianin's compound sometimes came out of solution and formed a separate liquid phase before solidifying. To avoid this a small crystal of Dianin's compound was left during the heating stage to act as a nucleating center.

The weight per cent uptake of hydrocarbons was determined by measuring the weight loss when a known weight of clathrate was sublimed at low pressure. In the case of pure hydrocarbon clathrates, results were expressed as mole ratios (Table 1). Some single crystal and powder diffraction x-ray studies were made on a few pure hydrocarbon clathrates* to establish the effect of guest component on unit cell dimensions (Tables 2 and 3).

The compositions of the hydrocarbon component of the clathrates prepared from mixtures were determined by melting the clathrates in a

TABLE 3

Powder Diffraction X-Ray Data[a]

Clathrate	a(Å), hexagonal	c(Å), hexagonal	V(Å^3), hexagonal	a(Å), rhombohedral	α
Ethanol	26.946(9)	10.977(4)	6902	15.98	114°56′
Benzene	27.23 (4)	10.94 (1)	7022	16.14	115°04′
o-Xylene	27.01 (3)	10.90 (1)	6883	16.01	115°01′
m-Xylene	27.06 (2)	10.91 (1)	6916	16.04	115°01′
p-Xylene	27.38 (9)	10.85 (5)	7044	16.22	115°10′
Toluene	27.28 (3)	10.83 (1)	6983	16.16	115°10′
Ethylbenzene	27.25 (3)	10.81 (1)	6952	16.14	115°10′

[a] Powder data collected in 114.6 mm diameter camera using CrKα (δ = 2.29092 Å) radiation. Cell parameters calculated and refined by a program due to Lindquist and Wengelin (*19*). Standard deviations shown in brackets refer to last decimal place.

* Slow cooling was necessary during the preparation of *o*-xylene, *m*-xylene, and 1,3,5-trimethylbenzene clathrates to obtain satisfactory crystals for single crystal studies.

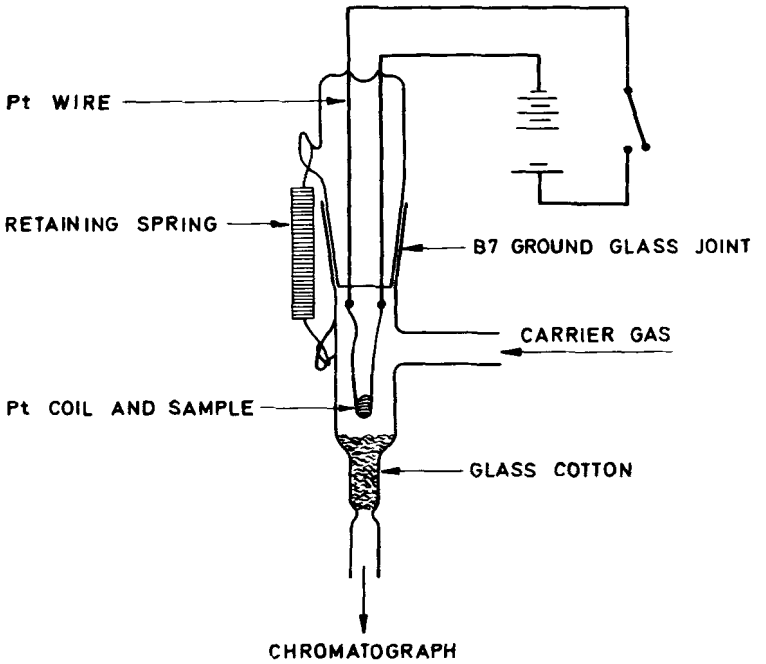


FIG. 1. GLC precolumn assembly.

small electrically heated platinum coil situated in the inlet of a capillary gas chromatograph (Fig. 1). The escaping hydrocarbons were swept via a stream splitter onto a squalane-coated capillary column. Weight percentages were calculated by direct normalization procedures, it being assumed that the relative response factors for the detector (flame ionization) used were unity.

During the course of this investigation variations were found in the mole ratios and selectivities observed for the same hydrocarbon or same hydrocarbon blend. Preliminary results indicated that these variations may be caused by differences in the rates of crystallization. Brief investigations were therefore made to study the effect of rate of cooling on mole ratio of the *n*-octane clathrate and the selectivity of Dianin's compound when crystallized from an equivolume blend of *n*-heptane and 2,4-dimethylpentane. The effect of blend composition on the composition of the hydrocarbon components of the clathrate was examined for the hydrocarbon pairs *n*-heptane/3-methylhexane, *n*-heptane/2,4-dimethyl-

pentane, 3-methylhexane/2,4-dimethylpentane, and *m*-xylene/ethylbenzene.

X-RAY INVESTIGATIONS

The preliminary x-ray investigations by Powell and Wetters (*13*) showed that Dianin's compound and its clathrates crystallize in the rhombohedral system with hexagonal cell dimensions $a = 27.0$ Å and $c = 11.1$ Å. The space group was $R\,\bar{3}$ and they suggested, by analogy

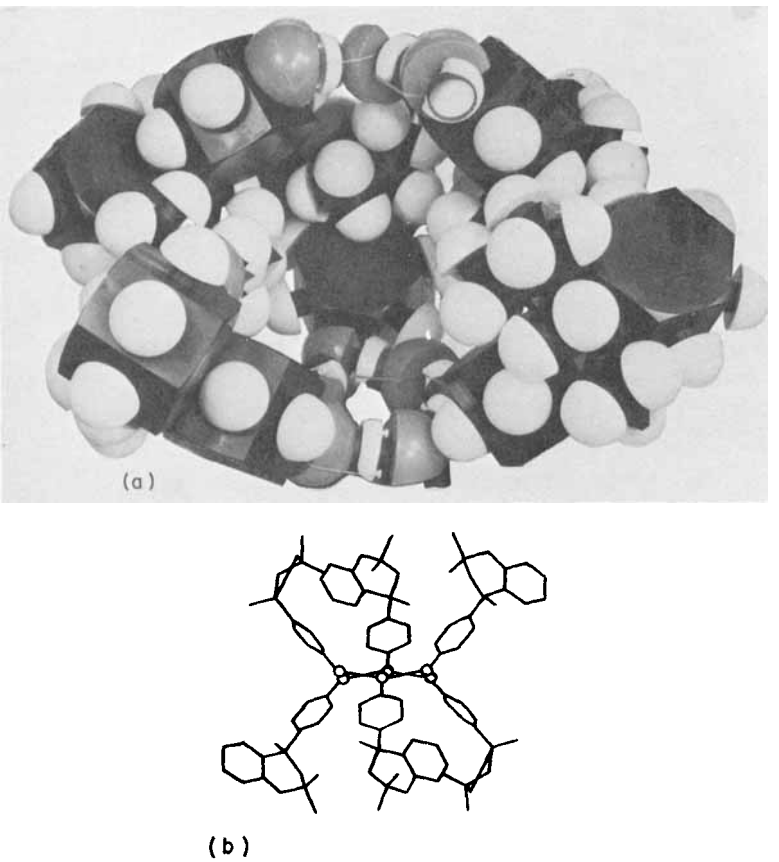


FIG. 2. (a) Model of Dianin's compound with one molecule removed showing detailed structure of the cage. (b) Basic structural unit (after Ref. *15*).

with the more extensively studied β-quinol clathrates, that the most likely structural unit comprised six molecules of Dianin's compound linked by a hexagon ring of hydrogen bonded OH groups with three molecules in threefold symmetry pointing upwards and the alternate three (enantiomorphs) pointing downwards. The downward pointing triplet from one OH-ring interleave with the upward pointing triplet from another OH-ring to form a cage, the height of which is equivalent to the *c*-axis of the hexagonal cell. Our early investigations (*14*) using Patterson and Fourier synthesis of *h, k, O* data from ethanol and methyl iodide complexes confirmed that the hydroxyl oxygen atoms formed a hexagonal ring and showed the 0—0 distance was ~2.8 Å.

Recently the detailed structures of the ethanol and CCl_4 clathrates of Dianin's compound have been published by Flippen, Karle, and Karle (*15*). Their results are basically in agreement with Powell and Wetters' suggested structure. The OH-ring is not flat but has a slightly puckered chair form (Fig. 2), while the external form of the cage is that of a double frustum of rotation with the minor axis as *c* and an equatorial diameter of about 20 Å. The cages form an infinite string parallel to *c* by fusion of the OH-rings but are arranged in cubic close-packed fashion in the plane perpendicular to *c*. The internal surface of the cage has a shape resembling an hour-glass; the widest part occurring at approximately 0.3*c* and 0.7*c* with the neck at the midpoint of the *c* axis. The narrowing of the cage is entirely due to C-19 and its associated hydrogen atoms (Figs. 2 and 3). Using the data for the ethanol clathrate, we have calculated the boundary contours of the atoms forming the cage (Fig. 3). These show clearly that for the level 0.3*c*, where the cage is widest, there are regions e.g., between C-8 and O-1 and C-12 and C-14, where there are larger gaps in the shell of the cage. Similar gaps are also found between C-2 and H-19a and H-19a and H-19b at level 0.4*c*. These gaps play an important part in determining the selectivity of Dianin's compound.

Single crystal (Table 2) and powder diffraction (Table 3) data on pure hydrocarbon clathrates show small but definite changes in unit cell dimensions with the structure of the guest molecule. If the nonclathrated form of Dianin's compound is taken as the norm, it is seen that clathration of *n*-heptane results in a slight increase (0.12 Å) in the *a* dimension but no change in the *c* dimension. This most probably results from repulsion between the neck-forming hydrogen atoms of the cage and the hydrogen atoms of the guest. The branched chain paraffin clathrates show larger expansion in the *a*-axis with a reduction in *c* dimension. The effect is more pronounced with 3-methylhexane than with 2-methyl-

hexane or 2-methylheptane and in this case is almost certainly caused by repulsion between the hydrogen atoms at the neck and the bulky methyl groups situated midway along the paraffin carbon chain. Minor changes in the intensities of the reflections were noted in the diffraction patterns and are probably attributable to small changes in atomic coordinates of the host compound rather than from the guest components as these, like ethanol and CCl_4 (*15*), would be expected to exhibit appreciable vibrational and rotational disorder.

With aromatic hydrocarbon clathrates there is no obvious pattern to be noted about the cell parameters in relation to the shape of the guest. The diffraction patterns of benzene, *m*-xylene, and *o*-xylene clathrates show, however, in addition to minor variations in intensity of the kind observed with paraffins, a pronounced {44.0} reflection that is either absent or weak in the diffraction patterns from clathrates with paraffin guests. With 1,3,5-trimethylbenzene, on the other hand, the {44.0} reflection has become very weak. Investigations with atomic models show that aromatic hydrocarbons could be appreciably more firmly held

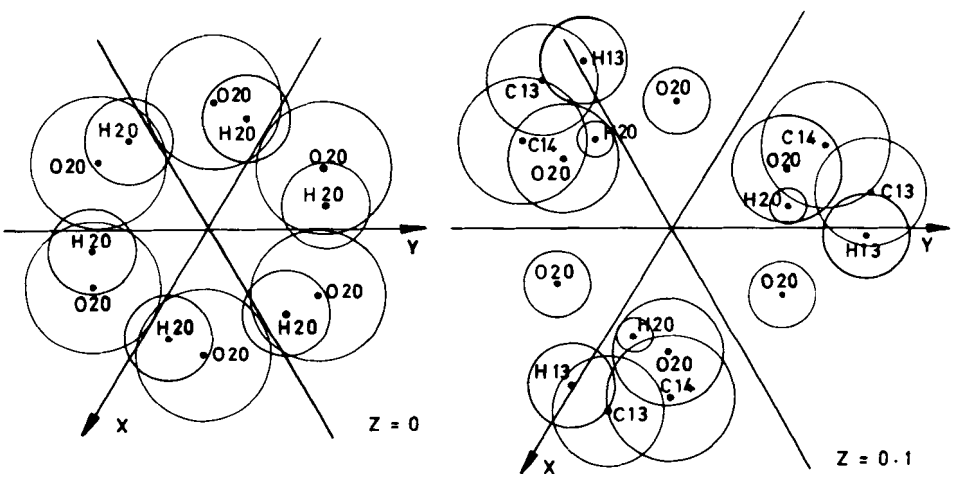


FIG. 3. Sections through the cage at levels 0 and 0.1 (above), 0.2 and 0.3 (page 800), and 0.4 and 0.5 (page 801) of the *c*-axis showing positions of those atoms which form the inside surface only. Atomic radii taken as 1.5 Å for aliphatic carbons, 1.4 Å for aromatic carbons, 1.5 Å for oxygen atoms, and 1.0 Å for hydrogen atoms.

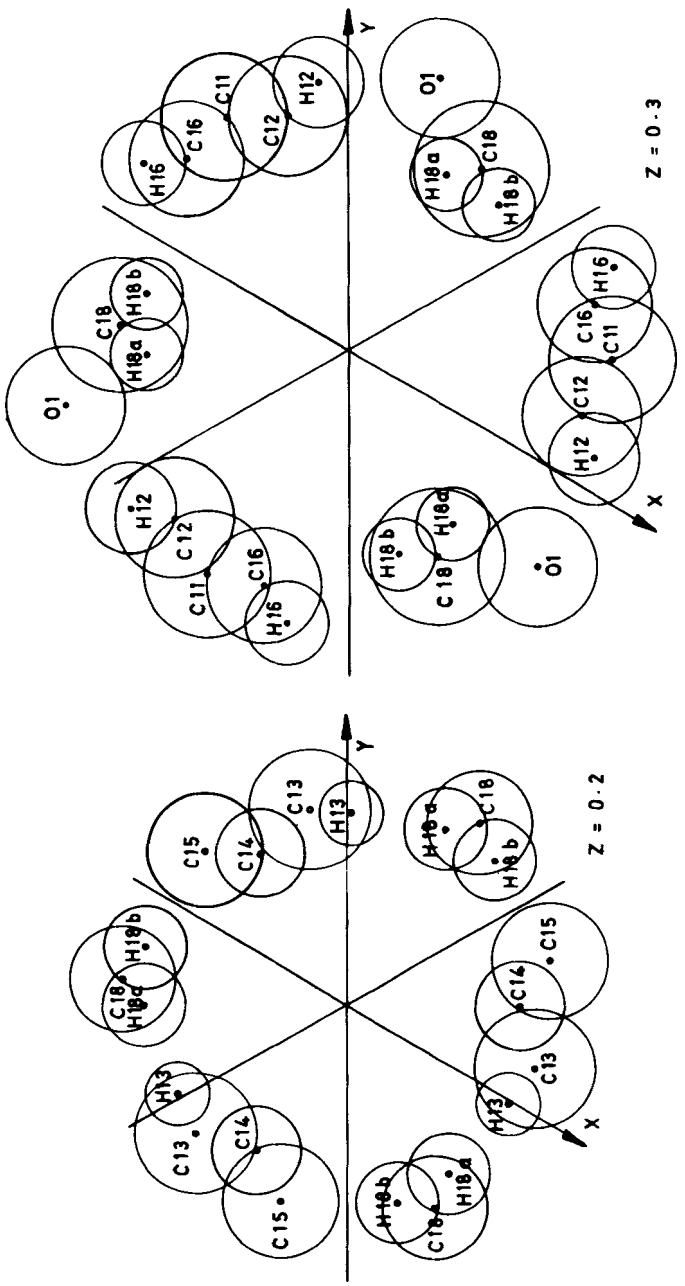


FIG. 3. See legend on page 799.

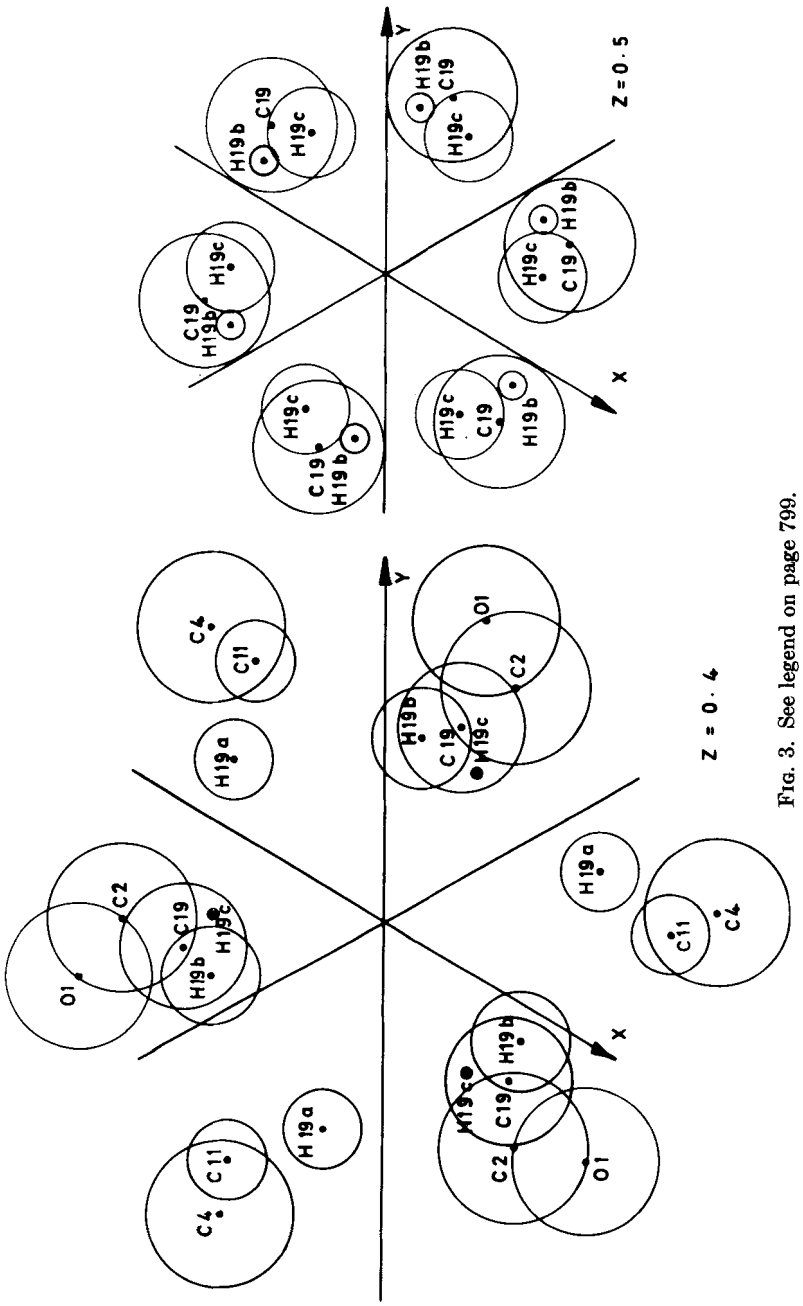


FIG. 3. See legend on page 799.

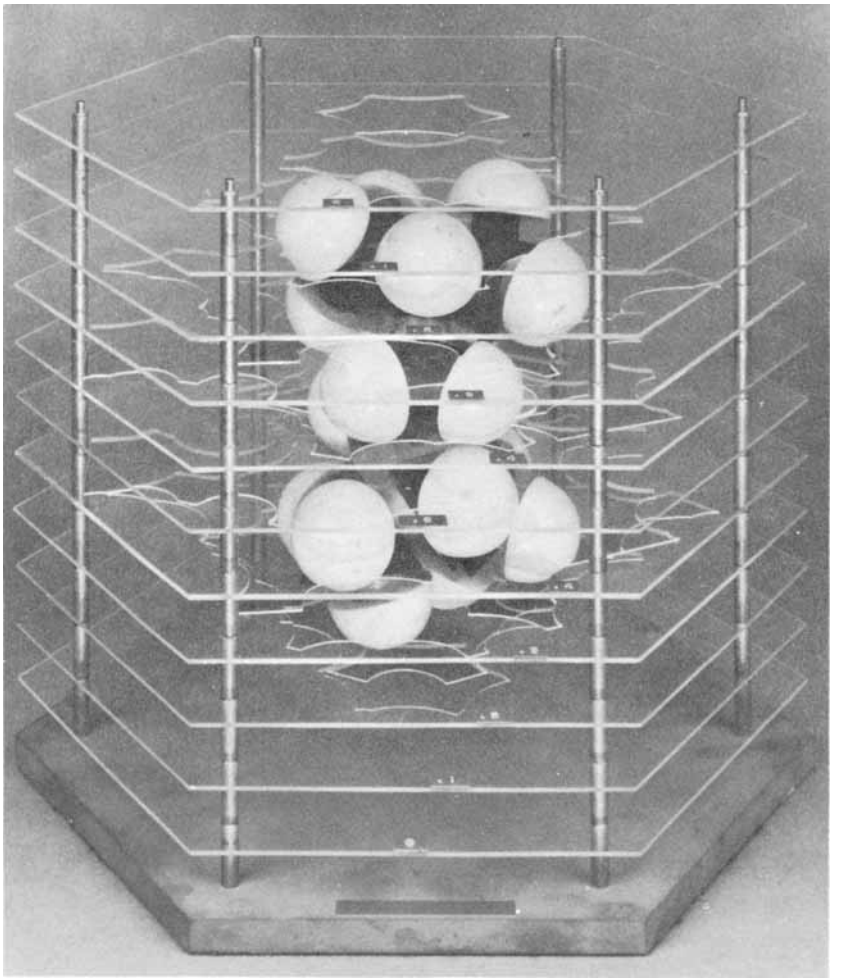


FIG. 4. Model of cavity constructed from data of Fig. 3. Guest component: 2,5-dimethylhexane.

in the cage and that small displacements in the host structure could lead to more ready accommodation of some of the more bulky aromatic hydrocarbons. Which of these factors is primarily responsible for the observed changes in intensity is at present unknown.

The analogous thiachroman to Dianin's compound (4-*p*-hydroxylphenyl-2,2,4-trimethylthiachroman) has recently been prepared (*16*) and shown to have a structure (*17*) similar to Dianin's compound.

RESULTS AND DISCUSSION

If all the cavities in Dianin's compound contain one guest molecule, the mole ratio of host:guest will be six. Complete occupancy of this kind, however, could only be expected if the guest molecule is readily accommodated in the cage and no appreciable repulsive forces between guest and host are invoked. From Flippen, Karle, and Karle's data it is obvious that many hydrocarbons could be accommodated without difficulty, and indeed this is reflected in the number of hydrocarbons that give mole ratios close to six (Table 1). Difficulty in clathration would be expected with hydrocarbons having lengths appreciably in excess of 10 Å or containing bulky substituents that interfere sterically with the methyl groups forming the "waist" of the cage. Results with the normal paraffins show that *n*-hexane and *n*-heptane are clathrated with ease, but at higher carbon numbers steric repulsion progressively increases until with *n*-decane well over 90% of the cages remain unfilled. Similarly the more bulky 2,2,4-trimethylpentane is less readily included than the isomeric *n*-octane, and the bulky 2,6-dimethyloctane is, as would be anticipated, almost totally rejected.

It would be convenient in discussing the selectivity of Dianin's compound to classify hydrocarbons according to their ease of accommodation. Since the amount of hydrocarbon included should be related to the ease of accommodation under specified conditions, it would seem appropriate to define an "accommodation factor" as the ratio of the observed to the ideal mole ratio. Thus, where ideally one guest molecule may be accommodated per cage,

$$\text{accommodation factor} = \frac{6}{\text{observed mole ratio (host:guest)}}$$

Initial attempts to investigate selectivity by determining the mole ratio of pure hydrocarbon clathrates gave poor reproducibility and also showed that there was only a very approximate correlation between the selectivity expected from the mole ratio data and that observed when Dianin's compound was crystallized from mixtures. With hydrocarbons that were clathrated with difficulty, i.e., tending to have mole ratios greater than six, there appeared to be some correlation between the percentage of hydrocarbon included and the rate of crystallization. Careful investigation with *n*-octane showed that the uptake of this guest molecule by Dianin's compound decreased as the rate of crystallization decreased (Table 4). The amount of hydrocarbon included is therefore dependent

upon *both* the dimensions of the guest molecule and the rate of formation of the cage. Comparison of accommodation factors is only valid providing they are determined under identical conditions of crystallization. This is difficult to control experimentally and we therefore turned our attention to mixtures.

The ratio of the number of moles N_i/N_r of two components I and R that will be taken up during crystallization of Dianin's compound from a mixture will be given by

$$N_i/N_r = (e^{-E_i/RT}/e^{-E_r/RT}) \int a_i\, dt \Big/ \int a_r\, dt$$

where a_i and a_r are the activities in the region of crystal growth and E_i and E_r are the activation energies of clathration. The ratio $e^{-E_i/RT}/e^{-E_r/RT}$, which represents the ease of clathration of component I to a reference component R, may be termed the "relative accommodation factor" thus,

$$\text{relative accommodation factor} = (N_i/N_r) \int a_r\, dt \Big/ \int a_i\, dt$$

If the activities of the components at the region of crystal growth are assumed equal to their activities in the bulk phase, and if clathration is carried out in the presence of a large excess of these reactants such that their activities may be assumed constant during clathration, then,

$$\text{relative accommodation factor} = (N_i/N_r)\ (a_r/a_i)$$

For the purposes of this investigation the activities of the reactants are assumed equal to their mole fraction x_i and x_r, hence

TABLE 4

Effect of Rate of Cooling on Mole Ratio of *n*-Octane Clathrate

Average rate of cooling over range 150 to 100°C[a] (°C/min)	Mole ratio Dianin's compound:*n*-octane
50 (estimated)	7.5
10	7.5
1.4	10.5
0.3	10.5

[a] 0.1 g Dianin's compound in 0.2 ml *n*-octane.

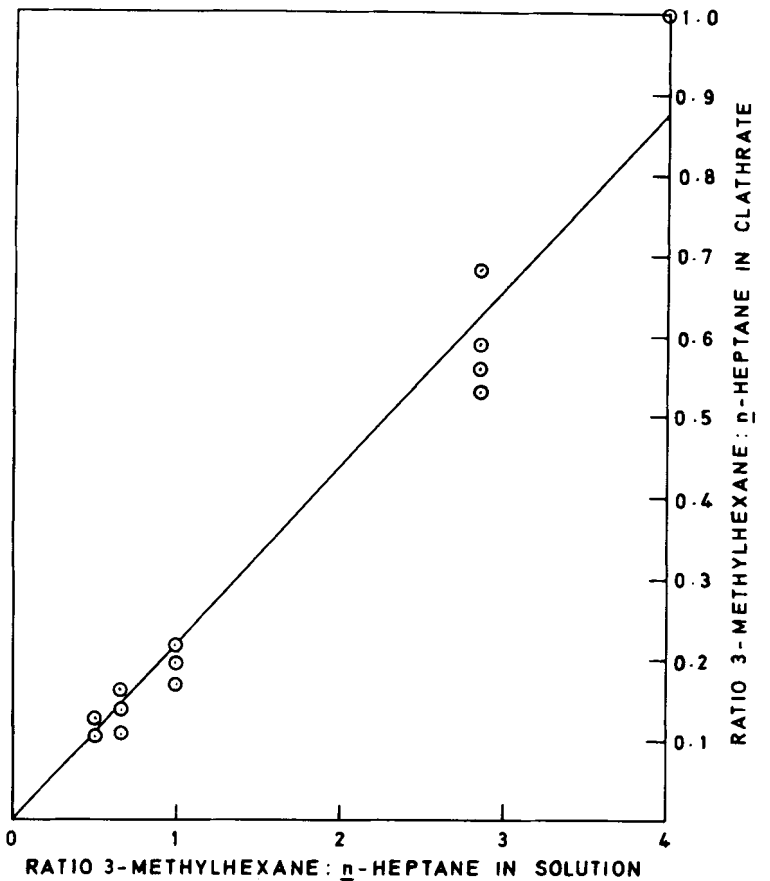


FIG. 5a. Plot of the composition of hydrocarbon component of the clathrates as a function of the composition of the solvent for the hydrocarbon mixture 3-methylhexane/*n*-heptane.

$$\text{relative accommodation factor} = (N_i/N_r)\ (x_r/x_i) = (W_i/W_r)\ (w_r/w_i)$$

where W_i and W_r are the weights of components I and R in the clathrate, and w_i and w_r their respective weights in the mixture from which clathration occurred.

Figures 5a, 5b, and 5c are plots of the composition of hydrocarbon component of the clathrates as a function of the composition of the solvent obtained for the binary hydrocarbon mixtures 3-methylhexane/*n*-heptane, 2,4-dimethylpentane/*n*-heptane, and 3-methylhexane/2,4-di-

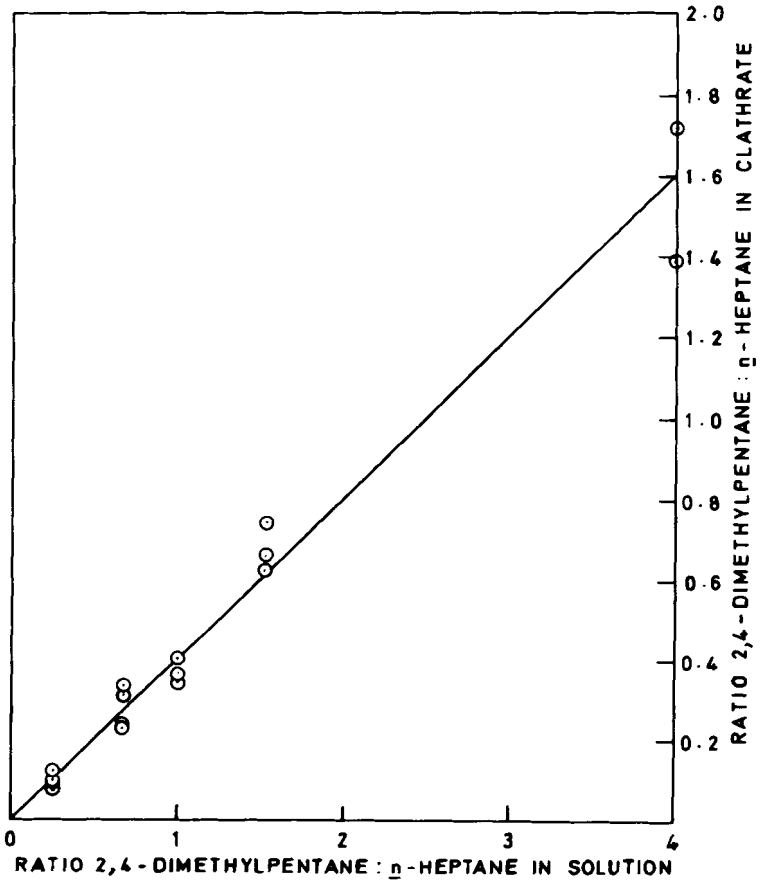


FIG. 5b. Plot of the composition of hydrocarbon component of the clathrates as a function of the composition of the solvent for the hydrocarbon mixture 2,4-dimethylpentane/*n*-heptane.

methylpentane. The relative accommodation factors for 3-methylhexane and 2,4-dimethylpentane to *n*-heptane are 0.22 and 0.40, respectively. The accommodation factor of 3-methylhexane relative to 2,4-dimethylpentane should be 0.22/0.40 = 0.55. This agrees within experimental error with the value 0.52 calculated from Fig. 5c. Similarly the ratio of components in the clathrate prepared from an equimolar blend of *n*-heptane/2,4-dimethylpentane/3-methylheptane would be expected to

be in the ratio of their relative accommodation factors. The observed values were 1:0.37:0.19. By extending the procedure it should be possible to calculate the composition of the hydrocarbon component of clathrates prepared from multicomponent mixtures from a knowledge of the activities or concentrations and relative accommodation factors of the individual hydrocarbons.

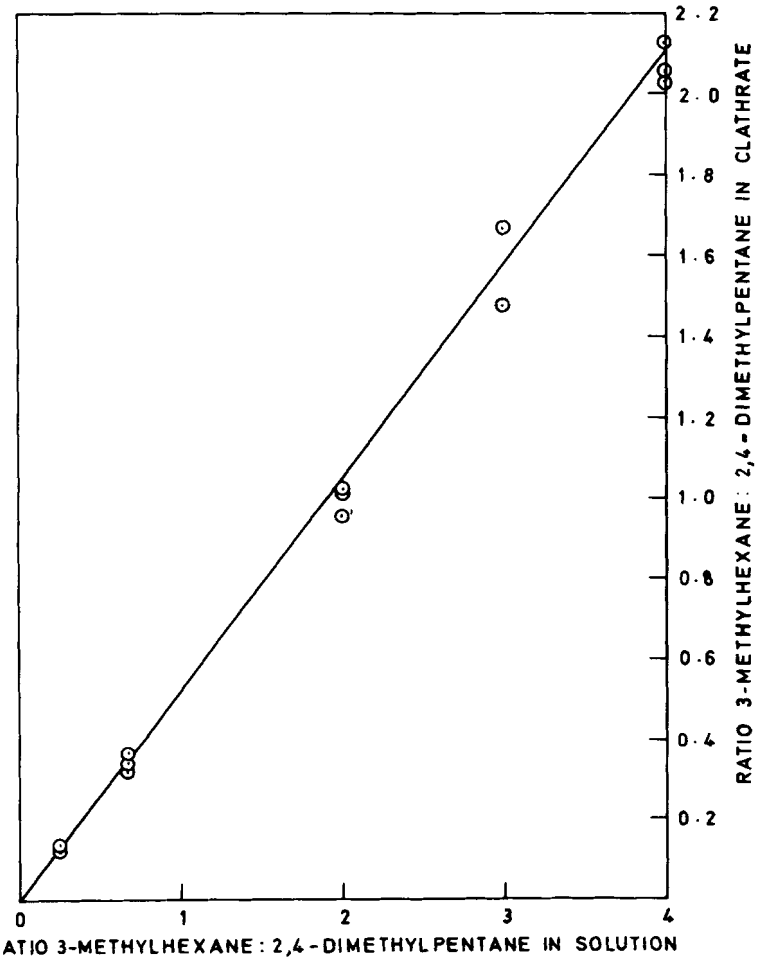
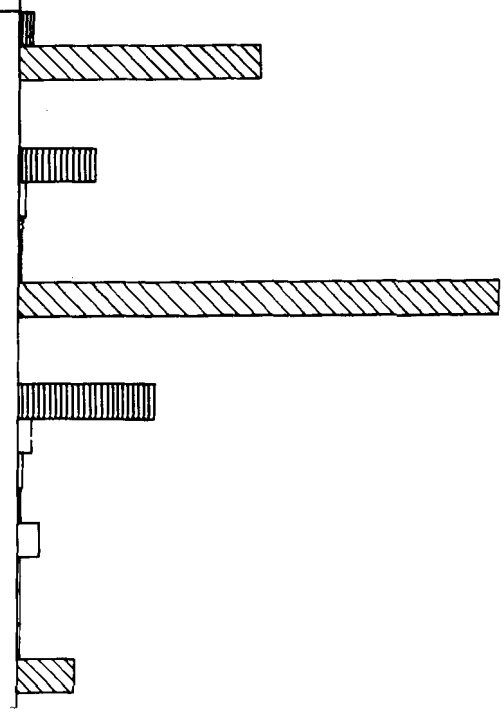


FIG. 5c. Plot of the composition of hydrocarbon component of the clathrates as a function of the composition of the solvent for the hydrocarbon mixture 3-methylhexane/2,4-dimethylpentane.

	Boiling Point °C	Relative Accomodation Factor (n-C_7=1)
Pentanes		
2-Methylbutane	27.85	0.23
n-Pentane	36.07	4.5
Hexanes		
2-Methylpentane	60.27	1.4
3-Methylpentane	63.28	0.1
2,2-Dimethylbutane	49.74	< 0.01
2,3-Dimethylbutane	57.99	< 0.01
n-Hexane	68.74	9.0
Heptanes		
2-Methylhexane	90.05	2.5
3-Methylhexane	91.85	0.22
2,2-Dimethylpentane	79.20	0.05
2,3-Dimethylpentane	89.78	< 0.01
2,4-Dimethylpentane	80.50	0.40
3,3-Dimethylpentane	86.06	< 0.01
2,2,3-Trimethylbutane	80.88	< 0.01
3-Ethylpentane	93.48	< 0.01
n-Heptane	98.43	1.00



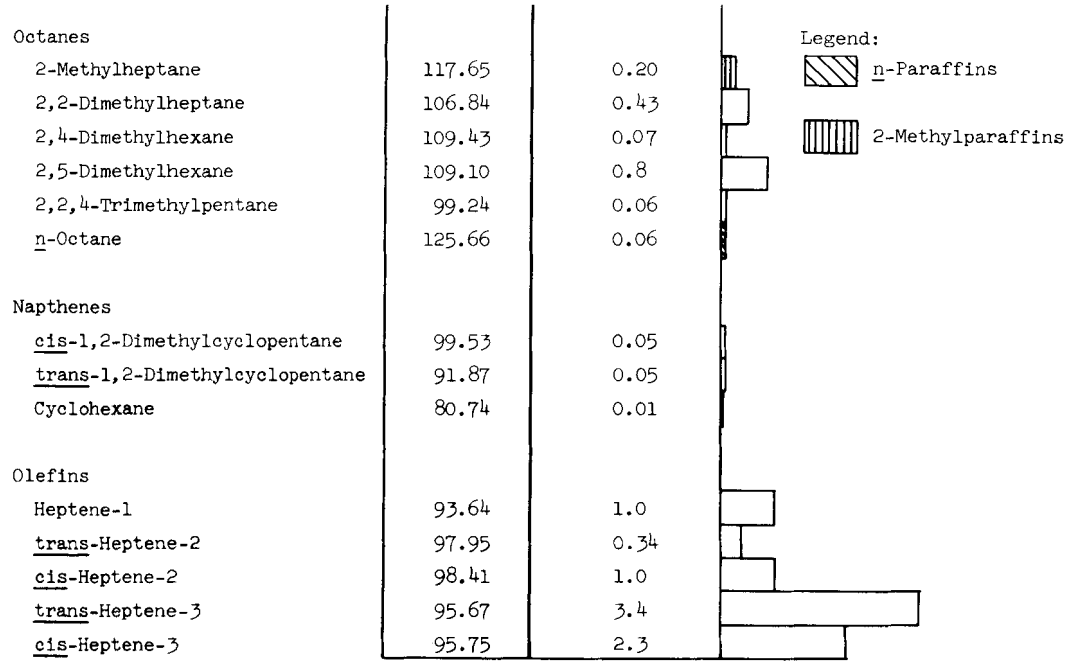


FIG. 6. Relative accommodation factors for paraffins, napthenes, and olefins in Dianin's compound.

Attempts to determine relative accommodation factors using single determinations of binary blends of hydrocarbons were not particularly successful because appreciable scatter was found in the composition of the hydrocarbon component of the clathrates prepared from the same hydrocarbon blend (cf. Figs. 5a, 5b, 5c). Investigations with an equimolar blend of *n*-heptane/2,4-dimethylpentane showed again the rate of crystallization was important.

The relative accommodation factor for 2,4-dimethylpentane varied from 0.56 at extremely high rates of crystallization (obtained by plunging the hot, sealed tube containing the components and dissolved Dianin's compound into ice water and agitating rapidly) to 0.22 when crystallization occurred very slowly. The results of this study (Table 5) also indicate that the relative accommodation factor approaches a limiting value at low rates of crystallization. This may also be accompanied by a decrease in the percentage uptake of hydrocarbon. Since the prime objective of this study was to obtain an indication of the separations that could be effected under process conditions, we did not investigate clathration characteristics of Dianin's compound at low rates of crystallization but rather chose an arbitrary cooling rate of around 5°C/min. Fully appreciating the limitations of this approach, we compiled the list of relative accommodation factors shown in Fig. 6. From this figure it is readily seen that Dianin's compound exhibits a marked selectivity during clathration from hydrocarbon mixtures, and it is interesting to consider this selectivity in the light of the recent structure determination of Flippen, Karle, and Karle (*15*).

TABLE 5

Effect of Rate of Cooling on Selectivity from Equivolume Blend of 2,4-Dimethylpentane and *n*-Heptane

Average rate of cooling over range 150 to 100°C (°C/min)	Composition of hydrocarbon component of clathrate (wt-%)		Relative accommodation factor (*n*-heptane = 1)
	n-Heptane	2,4-Dimethylpentane	
50 (estimated)	64.2	35.8	0.56
10	71.6	28.4	0.40
0.30	80.6	19.4	0.24
0.08	82.0	18.0	0.22

The most noticeable feature of the results presented in Fig. 6 is that the linear paraffins C_5–C_7 are readily included and that hydrocarbons containing one or more methyl groups at C-3 are almost totally rejected. Our earlier experiments suggested to us that the cage had a restriction midway along the *c*-axis and it was indeed satisfying when Flippen, Karle, and Karle first reported (*15*) their x-ray findings and referred to the "waist" in the cage formed by inwardly directed methyl groups. Immediately after we obtained details of the atomic coordinates we calculated the boundary contours (Fig. 3) of the atoms determining the cage dimensions and prepared a scale model (Fig. 4) of the cage to compare the ease with which atomic models of various hydrocarbons could be accommodated. Qualitatively our selectivity data for paraffin mixtures agreed very well with that anticipated from the model.

The long dimension of the cage is ca. 10.9 Å (Tables 2 and 3) and this is of a similar order to the extended length of *n*-hexane. This molecule may be accommodated in the cage without invoking any appreciable strain or restriction to free rotation, and clathration would appear to be particularly easy. Similarly *n*-pentane is also readily clathrated but the loss of a methylene group would lead to a reduction in the interaction energy between guest and host and accounts for the lower relative accommodation factor compared to *n*-hexane. Insertion of a methylene group into the hydrocarbon backbone of *n*-hexane brings the terminal methyl groups into close association with the top and bottom of the cage, and our model indicated that *n*-heptane could only be accommodated providing it was given a slight twist. *n*-Octane required more extensive coiling, and it seemed unlikely that this molecule could be included without incurring appreciable repulsion between the guest and cage. The observed marked decrease in relative accommodation factor in passing from *n*-hexane to *n*-octane therefore results principally from increased steric repulsion.

The selectivity among branched hydrocarbons follows a particularly interesting pattern that again may be accounted for in terms of the "hour-glass" structure of the cage. Among the dimethylpentane isomers, 3,3-dimethylpentane has the lowest relative accommodation factor since inclusion would invoke severe steric repulsion between the methyl substituents and the waist-forming methyl groups of the cage. 2,3-Dimethylpentane is also included with difficulty and for similar reasons 3-ethylpentane and 2,2,3-trimethylbutane have low relative accommodation factors. The presence of methyl groups at the C-2 and C-4 positions along the pentane backbone incurs appreciably less strain

during clathration and apart from 2-methylhexane, 2,4-dimethylpentane is the most readily accommodated branched heptane isomer. Molecular models show that even with the latter hydrocarbon some steric repulsion probably arises between the terminal methyl groups and the inwardly directed methyl groups of the cage. 2,5-Dimethylhexane, on the other hand, would not be restricted in this way and, as the results in Fig. 6 show, its relative accommodation factor is higher than 2,4-dimethylpentane or indeed the isomeric 2-methylheptane.

Relatively few selectivity studies were made with naphthenes and olefins. Clathration of naphthenes, apart from cyclopentane and possibly methylcyclopentane, is difficult due to their bulky spherical shape. Among the linear heptenes the *cis*- and *trans*-heptene-3 which have a small cross-sectional area approximately midway along the carbon backbone are most readily included. The selectivity pattern for olefins would almost certainly be similar to that of the paraffins with molecular shape being the dominant factor.

Studies with aromatic hydrocarbons (Fig. 7) show some selectivities that would be expected from the cavity dimensions based on Flippen, Karle and Karle's findings. Thus for the series of linear alkyl benzenes the maximum relative accommodation factor occurs with ethyl benzene. This molecule fits easily into the cage and the addition of a further methylene group in the alkyl chain (giving *n*-propylbenzene) leads to a less readily accommodated molecule than if the group were placed in an iso-position (giving isopropylbenzene). Generally, however, the selectivity of Dianin's compound for aromatic molecules cannot simply be accounted for in terms of the cage dimensions reported by Flippen, Karle, and Karle. For instance, the marked preference for *m*-xylene over *p*-xylene would not be expected and indeed mesitylene, one of the most readily accommodated aromatics, would hardly be expected to be taken up at all. To some extent small variations in atomic dimensions of the host structure may account for the observed selectivities. Flippen, Karle, and Karle found small differences in the atomic coordinates of the ethanol and chloroform clathrates and our own x-ray investigations show that small but definite differences in both unit cell dimensions and diffraction intensities occur from one aromatic clathrate to another. However, although atomic dimensions of the host are very important in determining selectivity, other factors may also contribute. Differences in basicity are believed to be responsible in part for the selectivity observed with Werner complexes of aromatic hydrocarbons (*9*, *18*), but it seems less likely that basicity is important in deciding the selectivity of Dianin's

	Boiling Point °C	Relative Accomodation Factor (nC_7=1)
C_6		
Benzene	80.10	0.15
C_7		
Toluene	110.62	0.20
C_8		
Ethylbenzene	136.19	0.54
p-Xylene	138.35	0.25
m-Xylene	139.10	0.54
o-Xylene	144.41	0.10
C_9		
iso-Propylbenzene	152.39	0.25
n-Propylbenzene	159.22	0.22
1-Methyl-3-ethylbenzene	161.31	0.80
1-Methyl-4-ethylbenzene	161.99	0.24
1-Methyl-2-ethylbenzene	165.15	0.21
1,3,5-Trimethylbenzene	164.72	0.64
1,2,4-Trimethylbenzene	169.35	0.17
1,2,3-Trimethylbenzene	176.08	0.13
C_{10}		
1-Methyl-3-isopropylbenzene	175.14	0.21
1-Methyl-4-isopropylbenzene	177.10	0.04
1-Methyl-2-isopropylbenzene	178.15	0.14

FIG. 7. Relative accommodation factors for aromatic hydrocarbons in Dianin's compound.

compound because of the more uniform electron density of the cage. Trapping of molecules during the formation of the clathrates, as suggested above, plays a role in controlling the selectivity among the paraffin hydrocarbons and would be expected to become very much more

important in controlling the clathration of rigid bulky aromatic molecules. Dynamic processes of this kind are difficult to study but may well be responsible for the high relative accommodation factor of mesitylene. Further studies are clearly required and in particular detailed x-ray studies of pure aromatic hydrocarbon clathrates.

APPLICATIONS

The unique selectivity of Dianin's compound enable separations to be effected that would be extremely difficult by the more widely established methods of separation. The principal stages in a clathration process using this host compound are (a) formation of the clathrate in the presence of the feed, (b) separation of the nonclathrated components from the clathrate, and (c) decomposition of the clathrate and recovery of the guest component. For small laboratory scale separations Dianin's compound may be simply crystallized from the feed and the clathrate and nonclathrate separated by filtration. The clathrate may then be decomposed by melting or dissolution in a suitable solvent. Such a procedure could be scaled up using carrier solvents to assist the filtration (centrifugation) and washing stages. Alternatively a fixed-bed type operation could be adopted in which molten Dianin's compound (either alone or deposited on a porous support) is contacted with feed and then cooled. After freeing the solid clathrate from the nonclathrated component the temperature is raised to melt the clathrate and release the guest. The principal disadvantages in using clathrates for large scale separation are the large host:guest ratio and the relatively high costs associated with the isolation and recovery of the host and guest components. These disadvantages will tend to limit the application of Dianin's compound primarily to separations where its unique selectivity characteristics may be fully exploited to yield products of comparatively high value.

A glance at Fig. 6 reveals that there are a number of hydrocarbons having similar boiling points and markedly different relative accommodation factors, e.g., 2,4-dimethylpentane/2,2,3-trimethylbutane, 2,4-dimethylpentane/cyclohexane, 2-methylhexane/2,3-dimethylpentane, *n*-heptane/2,2,4-trimethylpentane, and 1-methyl-3-ethylbenzene/1-methyl-4-ethylbenzene. In general these pairs are difficult to separate by distillation, and since they contain no specific functional groups only marginal enhancement of the relative volatility is possible by azeotropic

or extractive distillation. Such cases are obvious candidates for separation by clathration. A particularly attractive case would be the separation of 2-methylhexane (bp 90.05°C) from 2,3-dimethylpentane (bp 89.78°C). These hydrocarbons have a relative volatility of 1.008 and their separation by distillation would require several hundred plates. The relative accommodation factor of 2-methylhexane in Dianin's compound is over 200 times greater than that of 2,3-dimethylpentane and therefore 99% pure 2-methylhexane could be recovered from an equal weight feed by a single stage clathration. Clathration may also be used to scavenge trace impurities from relatively pure hydrocarbons. For instance, crystallization of Dianin's compound from 2,2,3-trimethylbutane (bp 80.88°C) will remove the close boiling impurities 2,2-dimethylpentane (bp 79.20°C) and 2,4-dimethylpentane (bp 80.50°C). This ability to selectively clathrate impurities emphasizes the importance of establishing the identity of the guest component during clathration studies even when using relatively high purity materials. Although the main emphasis in this investigation has been directed towards paraffinic and aromatic hydrocarbons (principally due to the more ready availability of pure compounds), the few preliminary studies with olefins have demonstrated that similar selectivity characteristics occur also with this class of hydrocarbons. In view of the greater number of olefins and general increased complexity of separation, selective clathration with Dianin's compound could prove an extremely useful technique. Similarly many interesting separations may also be found among hydrocarbon derivatives as the basic lattice structure of Dianin's compound appears to remain relatively unchanged when clathration occurs from a wide range of organic solvents.

Applications of Dianin's compound are not limited to separation only. Now that the dimensions of the cage are known, clathration studies could provide a rapid method of establishing or confirming the structure of an unknown compound. In this application Dianin's compound would be used as molecular calipers. The clathrates of Dianin's compound are also remarkably stable. Some hydrocarbon clathrates have remained completely unchanged in the authors' laboratory for almost 10 years. Clathrates therefore provide a very convenient way of storing unstable or expensive chemicals, e.g., radiochemically labeled compounds or rare hydrocarbons. Their stability and ease of handling would make them convenient for preparing reference standards in analytical work, e.g., gas chromatography.

CONCLUSIONS

Dianin's compound is unique not only with respect to the wide range of organic compounds with which it will form complexes, but also in its selectivity when crystallized from hydrocarbon mixtures. With paraffin hydrocarbons it is possible to account for the selectivity in terms of the unusual "hour-glass" shape of the cage, but with many rigid aromatic molecules no such simple correlation appears to exist. Both the degree of occupancy of the cavities and the selectivity have been found to depend upon the rate of crystallization, and these effects require more detailed study. The principal applications of Dianin's compound will be for specialized separation of compounds having similar physical properties (apart from shape) where more conventional methods, e.g., distillation, become inapplicable.

The unique feature of Dianin's compound is undoubtedly its characteristic of retaining the host lattice structure in the absence of guest components. This demonstrates the stability of the host lattice and suggests that some simple derivatives of Dianin's compound should also form clathrates. Now that the atomic coordinates of the basic clathrate are known, it should be possible to modify the selectivity characteristics in a predetermined way and thus to some extent "tailor-make" host structures for specific separations. The extent to which this may be achieved is at present unknown but seems well worth investigation.

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