Chemical Perturbation and Lattice Instability in Molecular Crystals: Crystal Structures and Molecular Motions of 1,4-Dihalonaphthalenes

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To understand the effect of chemical perturbation (created by a change of substituent or by a chemical impurity) on crystal structure, the crystal structures of 1,4-dichloronaphthalene (DCN, $C_{10}H_6Cl_2$) and 1,4-dibromonaphthalene (DBN, $C_{10}H_6Br_2$) have been determined from three-dimensional X-ray diffraction measurements. Crystals of DCN are found to be monoclinic with cell dimensions $a = 13\cdot386$ (3), $b = 3\cdot9394$ (6), $c = 16\cdot693$ (6) Å and $\beta = 103\cdot20$ (2)° with four molecules per unit cell in space group $P2_1/c$. Crystals of DBN are also monoclinic but with eight molecules per unit cell in space group $P2_1/a$. The cell dimensions are $a = 27\cdot230$ (13), $b = 16\cdot417$ (7), $c = 4\cdot048$ (2) Å and $\beta = 91\cdot95$ (2)°. Previous Raman results show that some dynamic interaction topology is preserved through the structure change. The X-ray analysis shows that the topology preserved is the molecular stacks parallel to the shortest axis in both structures and the retention of the DCN screw axis as a non-crystallographic screw axis in the DBN structure at $x = 0\cdot1216, y = 0\cdot3000$ and parallel to the c axis.

Introduction

A stable crystal structure represents the absolute minimum of the free-energy hypersurface in the lattice configuration space. The free energy of a dynamic lattice can conceptually be divided into two parts: (*a*) static and (*b*) dynamic. The static part arises from the intermolecular interaction in equilibrium geometry, while the dynamic part comes from non-trivial phonon motions. Both the static and dynamic parts of the free energy are functions of temperature, pressure and chemical composition. Changes in these parameters act as a perturbation on the free energy and can make the parent crystal structure unstable. Again, the instability in crystal structure caused by these perturbations can be of two types: (i) static instability which arises when, by the added perturbation, another equilibrium geometry of a lower free energy becomes available, and (ii) dynamic instability which occurs when the restoring force for a non-trivial phonon motion disappears owing to the perturbation. In each case a change in crystal structure results. In the case of a static instability, the crystal structure change usually follows a reconstructive path. In the case of a dynamic instability, the mode softening resulting from the lack of a restoring force leads to a displacive transition.

The crystal structure change following the lattice instability caused by temperature or pressure changes is called a phase transition and has been studied extensively. Phase transitions induced both by static instability and by dynamic instability are known to occur. The soft-mode mechanism characteristic of

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dynamic instability has been successfully applied to many phase transitions (Fleury, 1976, and references therein). The effect of a chemical perturbation on the crystal structure, and the nature of the lattice instability induced by this kind of perturbation have not been extensively explored. The present paper focuses on the nature of the lattice instability induced by a chemical perturbation in molecular solids. In a molecular solid the chemical perturbation can be created by successively changing a substituent group of the molecular unit or by adding a chemical impurity. Previous work (Prasad & Stevens, 1977) has shown that in the 1,4-dihalobenzene series the chemical perturbation and the thermal perturbation are distinct and almost independent. Furthermore, the chemical perturbation shows specificity in the effect of the position of a particular substituent group on the crystal structure (Chu & Prasad, 1977). In the present study the effect of chemical perturbation on crystal structure is examined for 1,4-dihalonaphthalenes. The 1,4-dihalonaphthalene series was selected because 1,4-dibromonaphthalene has attracted a great deal of interest from optical spectroscopists (Burland, 1976). It exhibits one-dimensional triplet exciton conduction (Hochstrasser & Whiteman, 1972), which results from linear stacking of these molecules in the observed crystal structure.

We discuss here the effect of chemical perturbation on the crystal structure in the series 1,4-dichloronaphthalene (DCN), 1-bromo-4-chloronaphthalene (BCN), and 1,4-dibromonaphthalene (DBN) by combining the present X-ray diffraction study with the Raman spectra of these compounds and their mixed crystals, presented elsewhere (Bellows & Prasad, 1977). The three-dimensional crystal and molecular structures

of DCN and DBN have been solved from single-crystal X-ray intensity measurements. The structure of DBN agrees with the previous solution in projection (Trotter, 1961).

Experimental

DBN was purchased from Eastman Organic Chemicals. The material was zone refined and recrystallized from ethanol yielding needles suitable for X-ray examination. DCN was synthesized by the Sandmeyer reaction from 1-chloro-4-aminonaphthalene (Aldrich Chemical Co.). It was sublimed yielding needles suitable for X-ray analysis.

DCN

The crystallographic and experimental data are summarized in Table 1. The structure was solved using Long's (1965) sign-predicting program. The 68 nor-

malized structure factors (E's) above 1.00 were used with a starting set of four permutable signs in addition to the three determining the origin. Only the Cl atom positions could be identified in the E map from the solution with the highest consistency index. However, using phases calculated from the Cl positions, the rest of the molecular skeleton could be identified in a Fourier synthesis.

After several cycles of least-squares refinement, H atoms were placed at predicted positions and included in the refinement. Anisotropic thermal parameters were refined for Cl, and isotropic thermal parameters for C and H. Scattering factors for Cl, C, and for a 'spherical bonded' H were taken from *International Tables for X-ray Crystallography* (1974). Final positional parameters are in Table 2.*

DBN

The crystallographic and experimental data are summarized in Table 1. Integrated intensities were obtained from analysis of the step-scan profiles (Blessing, Coppens & Becker, 1974), and corrected for Lorentz and polarization effects and for absorption by Gaussian numerical integration ($\mu = 47.7$ cm^{-1}). Positions of the four independent Br atoms were determined from the Patterson map with the aid of the two-dimensional structure solution (Trotter, 1961). Using the Br atoms to phase the reflections, all of the C atoms were located in a Fourier summation. Full-matrix least-

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* Lists of structure factors and thermal parameters for DCN and DBN have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33642 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Crystallographic data and experimental and refinement parameters for the crystal structures of 1,4-dichloronaphthalene (DCN) and 1,4-dibromonaphthalene (DBN)*

	DCN	DBN
Crystal data		
a (Å)	13.386 (3)	27.230 (13)
b (Å)	3.9394 (6)	16.417 (7)
c (Å)	16.693 (6)	4.048 (2)
β (°)	103.20 (2)	91.95 (2)
λ (Å)	0.71069 (Mo $K\bar{\alpha}$)	0.55941 (Ag $K\alpha_1$)
Space group	$P2_1/c$	$P2_1/a$
Z	4	8
D_{calc} (g cm^{-3})	1.527	2.101
D_{obs} (g cm^{-3})	1.52 (1)	2.08 (1)
Experimental and refinement data		
Crystal dimensions (mm)	0.2 × 0.5 × 0.2	0.15 × 0.40 × 0.33
Number of reflections		
Total measured	982	3832
Average		
$[I > 3\sigma(I)]$	245	1586
Data-collection mode	θ–2θ scan	θ–2θ scan
Instrument	Syntex $P2_1$	Picker FACS-1
Scan speed (deg min^{-1})	7.3	
Scan interval (°)		0.05
Counting interval (s)		1
Absorption correction	None	Gaussian numerical integration
μ (cm^{-1})	6.91	47.7
Final refinement cycles		
Number of reflections	245	1586
Number of variables	83	217
R	0.025	0.072
R_w	1.018	0.076
$w^{-2} = \sigma_I^2$	$\sigma_{count}^2 + (0.03I)^2$	$\sigma_{count}^2 + (0.03I)^2$

Table 2. 1,4-*Dichloronaphthalene: final fractional coordinates*

	x	y	z
Cl(1)	−0.0887 (1)	0.0866 (3)	0.2928 (1)
Cl(4)	−0.4889 (1)	−0.3493 (2)	0.3963 (1)
C(1)	−0.1987 (7)	−0.034 (1)	0.3234 (7)
C(2)	−0.2751 (8)	−0.187 (1)	0.2691 (9)
C(3)	−0.3658 (8)	−0.287 (1)	0.2906 (8)
C(4)	−0.3766 (7)	−0.225 (1)	0.3694 (7)
C(5)	−0.307 (1)	0.002 (1)	0.5102 (7)
C(6)	−0.2311 (9)	0.156 (1)	0.5664 (9)
C(7)	−0.1406 (9)	0.254 (1)	0.543 (1)
C(8)	−0.1257 (8)	0.194 (1)	0.4667 (8)
C(9)	−0.2059 (7)	0.036 (1)	0.4051 (7)
C(10)	−0.2977 (7)	−0.65 (1)	0.4301 (6)
H(2)	−0.273 (4)	−0.221 (8)	0.206 (4)
H(3)	−0.427 (4)	−0.413 (9)	0.251 (4)
H(5)	−0.370 (4)	−0.059 (9)	0.525 (3)
H(6)	−0.233 (5)	0.20 (1)	0.619 (4)
H(7)	−0.083 (4)	0.36 (1)	0.577 (4)
H(8)	−0.067 (4)	0.27 (1)	0.455 (5)

Table 3. 1,4-*Dibromonaphthalene: final fractional coordinates*

	x	y	z
Br(1-1)	0·10173 (6)	0·1448 (1)	0·3275 (4)
Br(1-4)	−0·06582 (7)	0·41137 (9)	0·6967 (5)
C(1-1)	0·0513 (5)	0·2187 (8)	0·441 (3)
C(1-2)	0·0575 (6)	0·2987 (9)	0·363 (3)
C(1-3)	0·0219 (7)	0·3555 (7)	0·438 (4)
C(1-4)	−0·0163 (6)	0·3310 (7)	0·590 (3)
C(1-5)	−0·0691 (5)	0·2233 (9)	0·846 (4)
C(1-6)	−0·0744 (5)	0·1449 (9)	0·927 (4)
C(1-7)	−0·0404 (6)	0·0868 (8)	0·836 (4)
C(1-8)	0·0019 (5)	0·1089 (8)	0·677 (3)
C(1-9)	0·0081 (5)	0·1921 (8)	0·596 (3)
C(1-10)	−0·0282 (5)	0·2490 (7)	0·680 (3)
H(1-2)	0·0849	0·3162	0·2572
H(1-3)	0·0259	0·4085	0·3876
H(1-5)	−0·0915	0·2602	0·8999
H(1-6)	−0·1010	0·1279	1·0333
H(1-7)	−0·0440	0·0330	0·8683
H(1-8)	0·0242	0·0710	0·6237
Br(2-1)	0·14182 (6)	0·45323 (9)	−0·1603 (4)
Br(2-4)	0·31112 (6)	0·18978 (9)	0·2979 (4)
C(2-1)	0·1926 (4)	0·3792 (8)	−0·015 (3)
C(2-2)	0·1857 (5)	0·2997 (6)	−0·092 (3)
C(2-3)	0·2220 (6)	0·2439 (8)	0·007 (3)
C(2-4)	0·2617 (5)	0·2678 (7)	0·171 (3)
C(2-5)	0·3123 (5)	0·3777 (8)	0·439 (4)
C(2-6)	0·3174 (5)	0·4593 (8)	0·521 (4)
C(2-7)	0·2812 (6)	0·5153 (8)	0·430 (4)
C(2-8)	0·2404 (5)	0·4917 (8)	0·253 (3)
C(2-9)	0·2336 (4)	0·4095 (7)	0·162 (3)
C(2-10)	0·2701 (5)	0·3502 (7)	0·260 (3)
H(2-2)	0·1588	0·2833	−0·2057
H(2-3)	0·2178	0·1909	−0·0418
H(2-5)	0·3350	0·3419	0·5010
H(2-6)	0·3439	0·4749	0·6388
H(2-7)	0·2851	0·5675	0·4845
H(2-8)	0·2178	0·5275	0·1885

squares refinement included anisotropic thermal parameters for Br and C, and H atoms at calculated positions. Final positional parameters are listed in Table 3.*

Results

The original object of the X-ray diffraction studies was to determine the packing structures of 1,4-dichloro- and 1,4-dibromonaphthalenes as an aid to interpreting their phonon spectra. Since highly accurate bond distances and angles were not necessary, diffraction data were collected rapidly. However, despite the speed with which data were collected, both structures were readily solved and refinement proceeded smoothly giving quite satisfactory agreement between observed and calculated structure factors.

Among the disubstituted compounds of naphthalene, the 1,4-disubstituted isomer is one of the least

* See previous footnote.
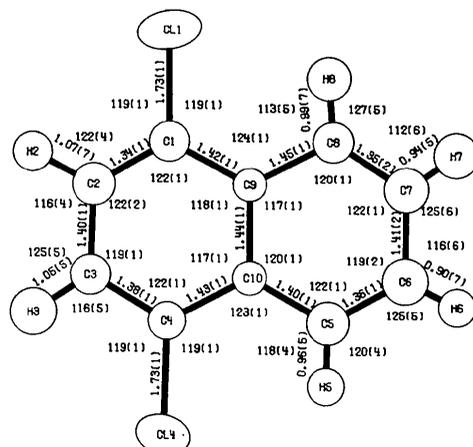
Fig. 1. Bond distances (Å) and angles (°) in DCN.
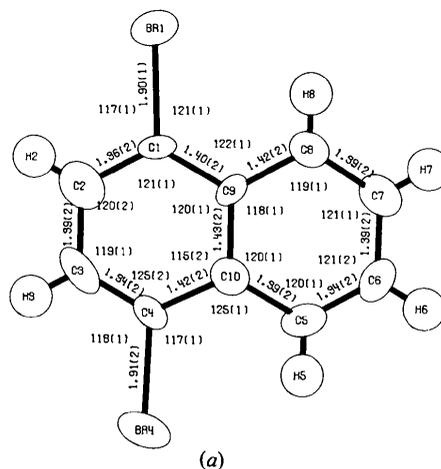
(a)
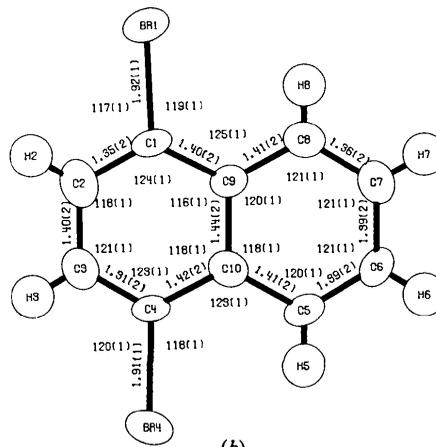
(b)

Fig. 2. Bond distances (Å) and angles (°) in DBN. (a) Molecule 1, (b) molecule 2.

studied by diffraction methods. The structure of 1,4-dihydroxynaphthalene has been reported by Gaultier & Hauw (1967). The geometry of the naphthalene ring system found in DCN and DBN is essentially the same

as in 1,4-dihydroxynaphthalene and rather similar to naphthalene itself. The bond distances and angles are shown in Figs. 1 and 2. Since they are not of primary importance to the study, they will not be discussed further.

As expected, the 1,4-dihalonaphthalene molecules of DCN and DBN are planar. The least-squares plane through the DCN molecule is given by the equation $0.4682x - 0.3514y + 0.3314z = 0.2531$. The only significant deviations from this plane are 0.022 (5) Å for C(10) and -0.07 (4) Å for H(2). Molecule 1 of DBN gives a least-squares plane of $0.1178x - 0.2500y$

$+ 0.3536z = 0.2717$ with significant deviations from the plane of 0.05 (2) Å for C(6) and -0.03 (1) Å for C(8). The least-squares plane through molecule 2 of DBN is given by $0.1357x + 0.2603y - 0.3517z = 0.3667$ with deviations of -0.04 (2) Å for C(2) and -0.05 (2) Å for C(3).

An analysis of the thermal motion of the molecules of DCN and DBN (Schomaker & Trueblood, 1968) indicates that the molecules are well described by rigid-body thermal motion. The r.m.s. difference between the observed U_{kj}'s and those calculated from the rigid-body model was 6.0×10^{-3} Å^2 for DCN, or about 10–15%
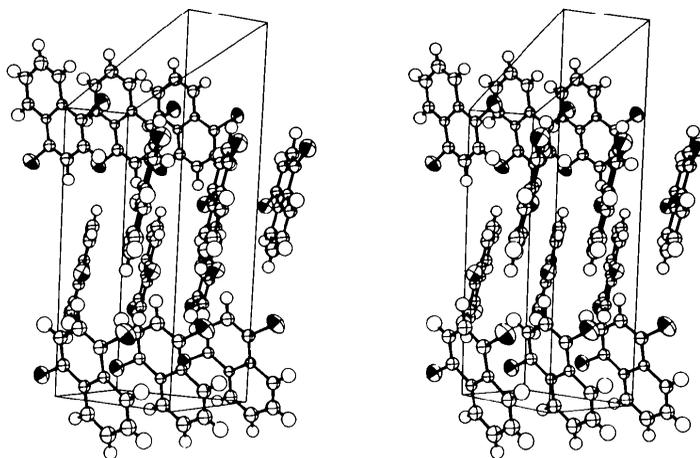
Fig. 3. Stereoscopic view of the crystal structure of DCN.
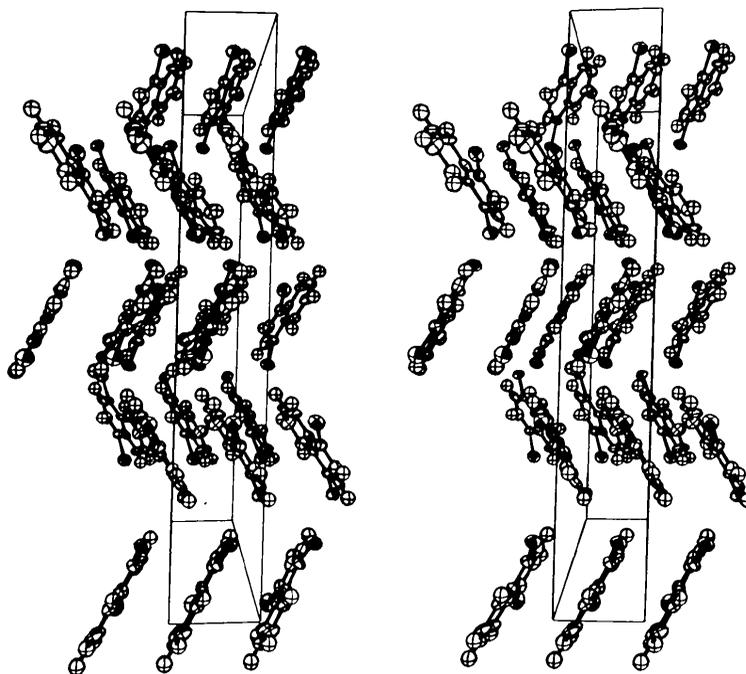
Fig. 4. Stereoscopic view of the crystal structure of DBN.

of the observed values. The corresponding r.m.s. differences for DBN were 7·2 and 6·4 × 10⁻³ Å² for molecules 1 and 2 respectively. Inclusion of a screw tensor in the rigid-body model did not significantly improve the fit.

Stereoscopic views of the structures of DCN and BCN are shown in Figs. 3 and 4 respectively. The presence of four molecules per unit cell in DCN is expected since the molecules do not have a center of inversion. The presence of eight molecules per unit cell in DBN is unusual since it requires two molecules per asymmetric unit. In both cases, the unit cell is part of a lamella of molecules generated by translation along the two longer axes of the cell. The important feature, however, is the stacks of molecules formed by the translation along the short axis. In DCN, the short axis is parallel to the twofold screw axis, but in DBN, the c axis is the short axis.

Discussion

To facilitate the discussion, we would like to summarize the chief results of the Raman study of the dihalo-naphthalenes (Bellows & Prasad, 1977). (1) DCN and BCN are isomorphous, but line-broadening indicated that BCN is orientationally disordered on the micro-scopic scale. (2) DBN has a different crystal structure. (3) Despite the different crystal structures, BCN and DBN form concentrated solid solutions. However, they exhibit a critical concentration region (24–44 mol% DBN) in which the structure changes from that of BCN to that of DBN. (4) Continuity of several phonon bands and of several crystal splittings of the internal vibrations as functions of composition in the BCN–DBN system reveals a continuity of dynamic interaction, implying that a certain interaction topology is maintained through the lattice instability. (5) From 4·2 K to the melting points no thermally induced phase transitions occur. (6) The phonon bands approach the critical concentration region with slopes which do not predict the softening of any optical mode in the region of lattice instability. The last two results imply that the lattice instability is static in nature.

Careful examination of the X-ray results can explain the Raman result that the topology of interaction is maintained through the change in crystal structure. Similar interactions between molecules in the stacks along the short axis would account for the continuity of the phonons across the critical concentration region. However, the continuous crystal splitting must arise from similar interactions between molecules in different stacks. The similarity is found to be in the relationship between the stacks related by the screw axis in DCN and within the asymmetric unit of DBN. The molecules of the asymmetric unit in DBN are related by a local non-crystallographic screw axis at $x = 0·1216$ (5), $y = 0·3000$ (1) parallel to the c axis with $\Delta z = 0·486$ (5).
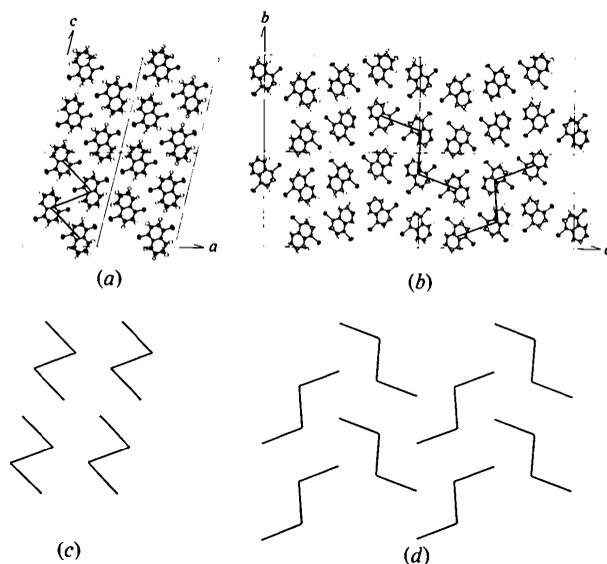
Fig. 5. Projection of (a) DCN in the ac plane and (b) DBN in the ab plane, showing the change in arrangement of screw-axis-related stack pairs. Repetition patterns are given for (c) DCN and (d) DBN.

Thus the screw axis in DCN is approximately retained in DBN, but is no longer a crystallographic symmetry element.

The differences between the crystal structures occur in the relationships among screw-axis-related pairs of stacks. In Fig. 5(a), a 'Z' is drawn through two sets of analogous molecules in DBN. It is clear that in DBN, the Z is extended. Furthermore, the stacking relation between Z's is altered between the two crystal structures. In DCN all the Z's are aligned, as shown in Fig. 5(c). In DBN, they form a lattice of nearly perpendicular alignments as shown in Fig. 5(d). The additional chemical perturbation of the DCN lattice by the second Br produces not a small distortion of the lattice, but a marked rearrangement.

The X-ray results on the DCN structure amplify the Raman results on BCN. Raman spectroscopy has indicated that BCN is isomorphous with DCN, but exhibits a microscopic orientational disorder presum-ably with respect to interchange of the Cl and Br position. The X-ray structure of DCN shows that Cl(1) is in a larger space than Cl(4), indicating that, due to energy considerations, the distribution of Cl and Br will not be completely random. No further study of the crystal structure of BCN is planned.

Our X-ray data reinforce the conclusion drawn from the Raman data that the lattice instability in the BCN–DBN system is static. The change from the DCN to the DBN structure requires a substantial rearrangement of molecules. All known soft-mode transitions represent small changes in orientation about a rotational axis, small displacements, or changes in long-range order (Hanson, 1975; McKenzie, 1975; Fleury, 1976). Since

Table 4. *Comparison of vibrational frequencies calculated from X-ray thermal parameters with observed Raman frequencies*

	Mean-square amplitude	v_{calc}
1,4-Dichloronaphthalene		
Translations	0·0514 (2) Å²	26 (1) cm⁻¹
	0·0314 (2)	34 (1)
	0·0198 (4)	43 (4)
Libration	0·0044 (4) rad²	35 (2)
	0·0041 (6)	45 (2)
	0·0026 (7)	75 (10)
v_{obs} (Raman, 77 K)	29·3, 36·0, 39·5 (sh),* 40·7, 49·4, 56·0, 59·0, 62·5, 66·4, 78·2, 84·3 cm⁻¹	
v_{obs} (Raman, 293 K)	24, 32, 42, 48, 58, 69, 76 cm⁻¹	
1,4-Dibromonaphthalene (molecule 1)		
Translations	0·046 (3) Å²	23 (1) cm⁻¹
	0·031 (3)	28 (2)
	0·027 (5)	30 (3)
Libration	0·0027 (5) rad²	33 (3)
	0·0036 (8)	33 (3)
	0·0015 (8)	96 (25)
1,4,Dibromonaphthalene (molecule 2)		
Translations	0·040 (2) Å²	25 (1) cm⁻¹
	0·033 (2)	27 (1)
	0·019 (4)	36 (3)
Libration	0·0022 (4) rad²	37 (3)
	0·0031 (6)	35 (3)
	0·0038 (7)	59 (5)
v_{obs} (Raman, 77 K)	17·1, 18·8, 21·9, 25·1, 26·5, 28·6, 31·1, 33·4, 35·0, 36·2, 38·4, 41·8, 47·5, 52·0, 63·4, 70·0, 87·2 cm⁻¹	
v_{obs} (Raman, 293 K)	18, 25, 28, 33, 35, 39, 47, 60, 66 (sh),* 82 cm⁻¹	

* sh = shoulder.

the change from the DCN to the DBN lattice requires a substantial rotation of an irregularly shaped molecule, a low-energy path between the two crystal structures is extremely unlikely. Structure changes should, therefore, occur by reconstructive mechanisms, which are characteristic of static lattice instabilities. Thus it may be concluded that chemical perturbation in the 1,4-dihalonaphthalenes produces static lattice instability.

Both X-ray diffraction and Raman (and other vibrational) spectroscopy provide information about molecular motions. Librational and translational frequencies calculated from thermal parameters for DCN and DBN according to Cruickshank's (1956) formula are given in Table 4, along with those observed in Raman spectra. Although some frequencies correlate

well with the room-temperature Raman values, the correlation is generally poor, especially when one considers the number of phonons resolved at lower temperatures. The discrepancy is expected, since the two techniques sample different aspects of the phonon motions.

In conclusion, we have found that the combination of X-ray and Raman data has aided the analysis of the chemical perturbation of the 1,4-dihalonaphthalenes. Thus, Raman spectroscopy reveals the preservation of certain dynamic interactions through the change of crystal structure, while X-ray diffraction reveals which interactions are preserved (stacking and local screw axis).

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