

# How to circumvent plastic phases: the single crystal X-ray analysis of norbornadiene

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The single crystal structure of the ordered phase of norbornadiene was determined using a new method of growing crystals at low temperatures, via an *in situ* technique utilising IR light from a CO<sub>2</sub> laser focused on a capillary filled with an organic solution of a sample that usually forms plastic crystals.

The properties of norbornadiene (bicyclo[2.2.1]hepta-2,5-diene), have been discussed extensively with respect to strain, conjugation and reactivity. The molecular structure has been investigated using spectroscopy,<sup>1</sup> gas electron diffraction<sup>2</sup> and theoretical calculations.<sup>3</sup> However, structural parameters from an X-ray analysis are hitherto unknown.

Norbornadiene is a molecule of globular shape<sup>4</sup> and thus tends to form plastic crystals which have in general unusually high melting points and very low entropies of melting (<21 J K<sup>-1</sup> mol<sup>-1</sup>).<sup>4</sup> Such plastic phases are orientationally disordered and do not permit acquisition of detailed structural data. Transitions to ordered low temperature phases are often observed upon further cooling; however, in most of the cases, the plastic crystals shatter during the phase transition. In these cases there are only a few methods available for obtaining a single crystal in the ordered low-temperature phase: (i) sublimation of the sample onto a cold finger cooled below the transition point; (ii) crystallization from a solution of the correct concentration such that saturation is reached at a temperature below the transition point; and (iii) using the shattered crystals of the low temperature phase as seeds and thus grow a single crystal by applying a high temperature gradient in a zone melting procedure. In order to circumvent the above problems, we report here a technique of crystal growth that allows direct access to low-temperature phases.

A DSC<sup>5</sup> investigation of norbornadiene revealed a melting point at -16.02 °C (lit.,<sup>6</sup> -19.1 °C) and a transition temperature at -64.23 °C. In the cooling diagram it solidifies at -19.66 °C and exhibits the phase transformation at -92.79 °C. According to the characteristics of plastic phases, the energy of melting is *ca.* five times lower than that of the phase transition.<sup>7</sup>

X-ray powder diffractograms, taken at different temperatures covering the range of the phase transition,<sup>8</sup> show the characteristics of the high temperature (HT) and low temperature (LT) phases (Fig. 1). The hexagonal lattice symmetry of the HT phase [ $a = b = 6.056(7)$ ,  $c = 9.711(12)$  Å, -33 °C] agrees with literature data.<sup>9</sup> The LT phase was indexed for a monoclinic cell [ $a = 6.291(2)$ ,  $b = 17.873(7)$ ,  $c = 5.157(3)$ ,  $\beta = 113.95(5)$ , -163 °C], in contrast to reported data which assumed a tetragonal cell.<sup>10</sup> The calculated densities for the HT

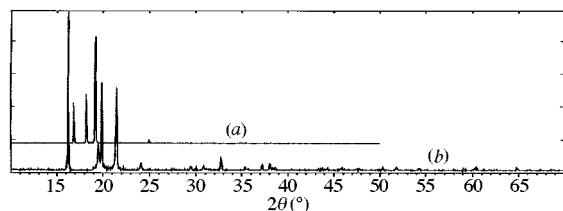


Fig. 1 X-Ray powder diffractograms of norbornadiene at (a) -33 and (b) -163 °C

and LT phases are 0.993 and 1.154 g cm<sup>-3</sup>, respectively. The density of the liquid, 0.906 g cm<sup>-3</sup>, is close to that of the HT phase and is in agreement with the expected properties for plastic phases.

In order to evade the HT phase, we modified the *in situ* technique utilizing a focused CO<sub>2</sub> laser beam on a capillary<sup>11</sup> such that, instead of filling the capillary with the neat material, we used an almost saturated solution. The main problems were to find an adequate solvent and an appropriate concentration in order to keep the point of saturation below the transition temperature. A wide variety of different solvents possessing very low melting points and/or low crystallization tendencies as well as good solubility properties were examined. Experiments with common solvents such as pentane failed; however, previous trials to crystallize 1,1-diethenylcyclopropane<sup>12</sup> (mp -131 °C) suggested that this liquid had the desired properties as it remained metastable (oily) down to -193 °C.

Gratifyingly, a 2:1 mixture of norbornadiene-1,1-diethenylcyclopropane produced a single crystal at -163 °C after a few refinement cycles, *i.e.* moving the CO<sub>2</sub> laser beam focus along the capillary over 12 h. The structure was determined by standard procedures.<sup>13</sup>

The most important geometrical parameters are given as mean values, based on the molecular symmetry C<sub>2v</sub>, in Fig. 2(a). Librational corrected data<sup>14</sup> together with a comparison of the experimental structural data and theoretical calculations are given in Table 1. The best agreement with the X-ray data is found for the MP2/6-31G(d) *ab initio* level<sup>15</sup> and the MW data.<sup>1</sup> Most remarkable are the lengths of the single bonds C1-C2, C1-C6, C3-C4 and C4-C5 [1.536(1) Å]; a value of 1.510 Å<sup>16</sup> would be expected for an sp<sup>2</sup>-sp<sup>3</sup> carbon bond. The same holds

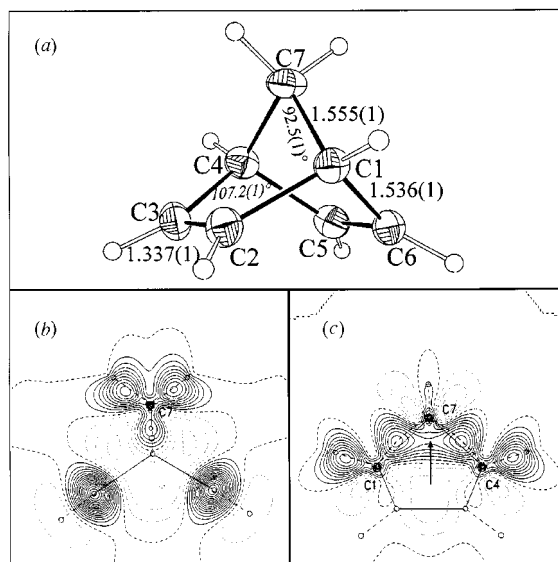


Fig. 2 (a) Molecular structure of norbornadiene with the most important bonding parameters. Probability plots 50%. (b) Static difference isoelectron density maps based on multipole refinements in the plane of (midpoint of C2-C3)-C7-(midpoint of C5-C6) and (c) in the plane of C1-C7-C4, distances at 0.05 e Å<sup>-3</sup>; zero line = broken, negative = dotted.

**Table 1** Comparison of experimental and calculated bond lengths and angles for norbornadiene; mean values according to  $C_{2v}$  symmetry (XRD: X-ray diffraction, this study; MW: microwave; GED: gas electron diffraction)

Method	Length/Å			Angle (°)		
	C1–C2	C1–C7	C2=C3	C1–C2–C3	C1–C7–C4	$\beta^a$
XRD	1.536(1)	1.555(1)	1.337(1)	107.2(1)	92.5(1)	4.5(2)
XRD <sup>b</sup>	1.542(1)	1.560(1)	1.342(1)			
MW <sup>c</sup>	1.530(3)	1.557(3)	1.336(3)	107.1(1)	91.9(2)	4.0(3)
NMR <sup>c</sup>	1.533	1.571	1.339	107.0	92.2	4
GED <sup>d</sup>	1.535(7)	1.573(14)	1.343(3)		94.1(30)	0
HF/ 6-31G(d)	1.539	1.550	1.319	107.7	92.3	2.7
MP2/ 6-31G(d)	1.533	1.552	1.345	107.0	92.3	3.7

<sup>a</sup> Interplanar angle between C1–C2–C3–C4 and H2–C2–C3–H3. <sup>b</sup> Librational corrected data, see ref. 14. <sup>c</sup> Ref. 1. <sup>d</sup> Ref. 2.

for the  $sp^3$ – $sp^3$  bonds between C1–C7 and C4–C7 [1.555(1) Å]; the expected value is 1.544 Å.<sup>16</sup>

In norbornadiene two different types of intramolecular interactions are assumed: homoconjugation, as a through space interaction between the two  $\pi$ -systems, and hyperconjugation, as a through bond interaction between the  $\pi$ -systems and the  $\sigma$ -frame.<sup>17</sup> The latter effect may explain the elongation of the single bonds because the filled  $\pi$ -orbitals of the double bonds have a destabilizing effect on the filled  $\sigma$ -orbitals of the opposite positioned single bonds. The double bonds [1.337(1) Å], however, are close to standard bond lengths (1.335 Å).<sup>16</sup>

Multipole refinements<sup>18</sup> with this data set permitted the production of two-dimensional experimental static electron density maps [Fig. 2(b) and (c)]. The double bond region in the plane intercepting the double bonds and C7 [Fig. 2(b)] shows the typical elliptic distortion. The section through the atoms C1, C7 and C4 [Fig. 3(c)] demonstrates the strain produced by the small angle at the bridgehead atom (see Table 1) as the maxima of the electron density of the bent bonds at C1–C7 and C4–C7 are clearly shifted from the internuclear lines. This is emphasized by the dashed interconnective lines [Fig. 2(c)]. Another interesting feature in Fig. 2(c) is the residual electron density at the internal part of the molecule (marked with an arrow). This electron density is similar to that found in the center of a cyclopropane molecule and which is attributed to  $\sigma$ -aromaticity and rehybridization by angular strain.<sup>19</sup>

Over the last 30+ years various theories have been introduced to describe the high reactivity and the *exo*-selectivity of bicyclo[2.2.1]alkenes compared to similar non-cyclic molecules. A reasonable explanation is the pyramidalisation of the double bonds.<sup>20</sup> The amount of pyramidalisation is described by the interplanar angle  $\beta$  between planes C1–C2–C3–C4 and H2–C2–C3–H3 H. The atoms at the double bonds are displaced to the *endo*-region of the molecule. The X-ray analysis gives  $\beta = 4.5(2)^\circ$  (Table 1). This value agrees well with the theoretically calculated ( $3.7^\circ$ ) and experimentally determined ( $4.0^\circ$ , by microwave and NMR spectroscopy) values.

Houk *et al.*<sup>21</sup> suggested the high frame strain as a cause for the pyramidalisation. An explanation for the direction of the pyramidalisation is not only strain alone, but also a contribution from a torsional interaction.<sup>21</sup> The results from our investigation suggest an additional repulsive effect of the hyperconjugation as the main cause for the pyramidalisation of the double bonds in the direction of the '*exo*' area. The effect of the pyramidalisation is expected to be even stronger for norbornene for which the *ab initio* calculations [MP2/6-31G(d)] predict an angle  $\beta$  of  $7.9^\circ$ .

In summary, molecular and crystal structures for a wide range of orientationally disordered materials should now be accessible with this new method. Crystal growth of the low temperature phase of similar molecules which form plastic crystals in the high temperature phases are in progress.

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## Notes and References

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