3,3-Dichloro-7-(2,2-dichlorovinyl)tricyclo[4.1.0.0^{2,4}]heptane, $C_9H_8Cl_4$

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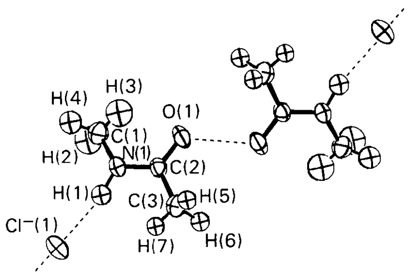

Fig. 1. 50% probability thermal ellipsoids of molecule (I) and the linkage resulting from the action of the binary axis and hydrogen bonds.

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3,3-Dichloro-7-(2,2-dichlorovinyl)tricyclo[4.1.0.0^{2,4}]heptane, $C_9H_8Cl_4$

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Abstract. $M_r = 258{\cdot}0$, monoclinic, $P2_1/c$, $a = 9{\cdot}418\,(2)$, $b = 10{\cdot}935\,(4)$, $c = 11{\cdot}272\,(2)$ Å, $\beta = 116{\cdot}31\,(1)°$, $U = 1040{\cdot}6$ Å^3, $Z = 4$, D_m(at 273 K) $= 1{\cdot}609\,(1)$, D_x(at 193 K) $= 1{\cdot}647$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 1{\cdot}05$ mm^{-1}, $F(000) = 520$. Final $R = 0{\cdot}031$ for 1611 observed reflections. The five-membered ring of the tricyclo[4.1.0.0^{2,4}]heptane moiety is planar with the two cyclopropane rings fused in an *anti* configuration relative to each other. The geometry of the three-membered rings is consistent with the electronic effects induced by their respective substituents.

Introduction. The unknown adduct (3) (Fig. 1) has been isolated (Jefford, Bernardinelli, Rossier & Zuber, 1982) from the reaction mixture between dichlorocarbene and bicyclo[2.2.1]hepta-2,5-diene (2). It was shown that the formation of (3) does not result from a rearrangement of standard adducts. Mechanistic significance of adduct (3) required definite proof of its structure with special emphasis on the configuration at C(7). Therefore (3) was converted stereospecifically into (1) by dichlorocarbene addition and the resulting adduct subjected to X-ray analysis. It is worth mentioning that the double adduct (1) was also isolated from the original carbene reaction mixture.

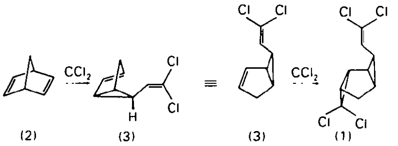

Fig. 1. Synthetic pathway for dichlorocarbene addition to 8,9,10-trinorbornadiene (2) giving the title compound (1).

Experimental. Colorless crystals of (1) grown by slow evaporation of a hexane solution at room temperature, m.p. = 322·7 K, D_m measured by flotation, elongated prism in a direction perpendicular to the unique axis, 0·30 × 0·20 × 0·22 mm; automatic four-circle Philips PW1100 diffractometer, graphite-monochromated Mo $K\alpha$; 32 reflections within range $25 \le 2\theta \le 33°$ used for measuring lattice parameters; no absorption corrections applied; $2\theta_{\max} = 24°$; range of *hkl*: $0 \le h \le 11$, $0 \le k \le 13$, $-13 \le l \le 12$; three standard reflections varied in intensity by <3% throughout data collection; 2029 reflections measured at 193 K, 1829 independent, $R_{\text{int}} = 0{\cdot}012$, 1611 structure amplitudes with $|F_o| > 3\sigma(F_o)$ considered observed and used in structure analysis; structure solved by direct methods using *SINGEN* and *TANGEN* programs of the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); full-matrix least-squares refinement on F; all H atoms located from a ΔF synthesis calculated at an intermediate stage of the resolution; calculations carried out with anisotropic temperature factors for non-H atoms and isotropic factors for H; final $R = 0{\cdot}031$, $wR = 0{\cdot}037$, $S = 0{\cdot}7173$; $w = 1$ for

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$|F_o| \leq 32$, $w = (32/F_o)^2$ for $|F_o| > 32$; ratio of maximum least-squares shift-to-error = 0·486; secondary extinction value not used; atomic scattering factors for C and Cl from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965).

Discussion. Final atomic and thermal parameters are listed in Table 1.* The atom-numbering system and the molecular geometry are reported in Fig. 2, and a stereoview of the molecule is shown in Fig. 3.

A five-membered ring fused with one or two cyclopropane rings forms a highly strained skeleton in either case. Our knowledge of the structural properties of such systems originates mainly from studies on bicyclo[3.1.0]hexane (4) and its derivatives, using techniques such as microwave spectroscopy (Cook & Malloy, 1974), electron diffraction (Mastryukov, Osina, Vilkov & Hilderbrandt, 1977) or X-ray diffraction (Grostic, Duchamp & Chidester, 1971; Morris, Murray-Rust & Murray-Rust, 1977). In molecules containing the framework (4) the five-membered ring adopts an envelope conformation such that a global boat form ensues with the fused cyclopropane. Addition of a second cyclopropane somewhat flattens the five-membered ring in tricyclo[4.1.0.0^{1,3}]heptane (5) where the half-chair conformation is observed (Smith, Andersen & Bunce, 1977), whereas *the cyclopentane unit of* (1) *is planar*. A similar arrangement of two cyclopropane rings 1,3-fused with a six-membered ring induces a corresponding flattening of the latter (Beintema, 1976). In (1), the dichlorinated and the vinyl-substituted cyclopropanes are both *cis*-fused to the five-membered ring and inclined to the mean plane at angles of 68 and 69° respectively. Their apical atoms, C(3) and C(7), are oriented in an *anti* configuration relative to each other. *cis*-fusion inhibits any significant departure from zero of the endocyclic torsional angles about C(1)–C(2) to C(6)–C(1), restricting their values to −1·2, 0·0, 1·2, −2·0 and 2·0°, respectively. The standard deviation of the ring atoms from the mean cyclopentane plane is 0·010 Å with a maximum deviation of 0·012 Å for C(6). The planarity induces, in the five-membered ring, an opening of the C–C–C bond angles to a mean value of 108·0°. This angle value is 105·0° in the corresponding non-planar ring of (5) (Smith *et al.*, 1977), and 104·5° in cyclopentane (Adams, Geise & Bartell, 1970). Moreover, the average

Table 1. *Fractional atomic coordinates and isotropic temperature factors* ($\times 10^3$) *with e.s.d.'s in parentheses*

U_{eq} (Å^2) = $\frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*(\mathbf{a}_i.\mathbf{a}_j)$.

	x	y	z	U_{eq}/U_{iso}
Cl(1)	0·47063 (8)	0·09287 (5)	0·85231 (6)	30 (1)
Cl(2)	0·67183 (7)	0·30794 (6)	0·92342 (6)	37 (1)
Cl(3)	0·10385 (9)	0·57304 (7)	0·27540 (7)	41 (1)
Cl(4)	−0·14469 (8)	0·40571 (7)	0·25023 (7)	46 (1)
C(1)	0·2039 (3)	0·2663 (2)	0·6645 (2)	28 (1)
C(2)	0·3651 (3)	0·3217 (2)	0·7266 (2)	22 (1)
C(3)	0·5005 (3)	0·2388 (2)	0·8019 (2)	23 (1)
C(4)	0·4612 (3)	0·2652 (2)	0·6604 (2)	25 (1)
C(5)	0·3571 (3)	0·1740 (2)	0·5567 (2)	33 (1)
C(6)	0·1977 (3)	0·1786 (2)	0·5593 (2)	34 (1)
C(7)	0·1031 (3)	0·2975 (3)	0·5193 (2)	34 (1)
C(8)	0·1454 (3)	0·3995 (2)	0·4561 (2)	30 (1)
C(9)	0·0484 (3)	0·4519 (2)	0·3439 (2)	29 (1)
H(1)	0·153 (3)	0·252 (3)	0·719 (3)	36 (7)
H(2)	0·381 (3)	0·405 (2)	0·757 (2)	24 (6)
H(4)	0·539 (3)	0·314 (3)	0·646 (3)	35 (7)
H(5)*A*	0·347 (3)	0·198 (3)	0·471 (3)	36 (7)
H(5)*B*	0·402 (4)	0·090 (3)	0·578 (3)	50 (9)
H(6)	0·131 (3)	0·396 (3)	0·037 (3)	41 (8)
H(7)	−0·007 (4)	0·289 (3)	0·489 (3)	50 (8)
H(8)	0·250 (3)	0·433 (3)	0·498 (3)	45 (8)

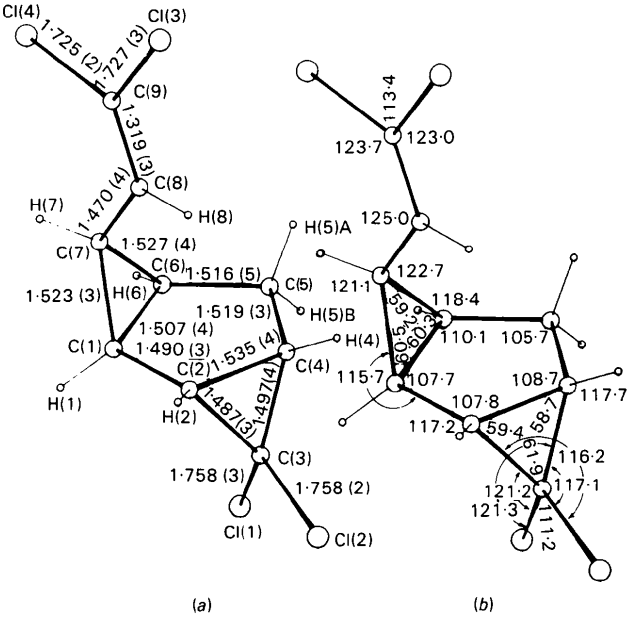

Fig. 2. Final geometry of the title compound. (*a*) Atom numbering and bond distances (Å) [the average C–H distance is 0·97 (3) Å]. (*b*) Bond angles (°) (standard deviations do not exceed 0·2°).

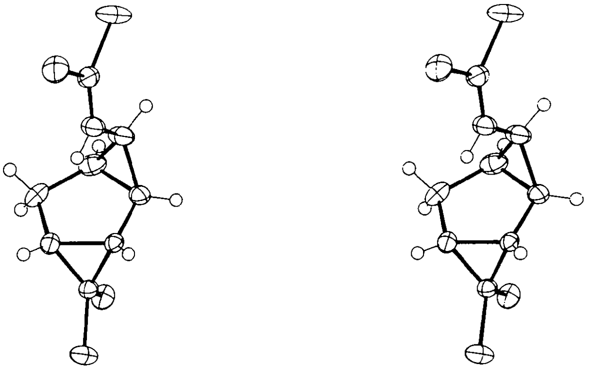

Fig. 3. Stereoscopic view of the title compound.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38281 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bond length of the five-membered ring of (1) [1·513 (17) Å] is shorter than that observed for (5) [1·530 (23) Å] or for cyclopentane [1·546 (1) Å].

It has been established that cyclopropane with its C($sp^{2.2}$) hybrid orbitals (Allen, 1981) can behave like a C=C double bond (Charton, 1970). In (1) the planarity of the five-membered ring and the 1,3-arrangement of the cyclopropanes allow a pseudoconjugation through C(6)—C(1)—C(2)—C(4) inducing a noticeable shortening of the central bond C(1)—C(2) [1·490 (3) Å]. The C(1)—C(6) and C(2)—C(4) bond lengths illustrate the substituent-induced effects on the equilibrium geometries of small rings (Hoffmann, 1971). The C(2)—C(4) bond appears to be significantly longer than the corresponding one in several other fused polycyclic compounds, whereas a concomitant shortening of the C(2)—C(3) [1·487 (3) Å] and C(3)—C(4) [1·497 (4) Å] bonds is worthy of note. This trend is consistent with the effect of π-donor substituents, here two *gem*-Cl atoms, as suggested by Hoffmann (1971). *Ab initio* calculations for 1,1-dichloropropane (Skanke, 1977) also support the experimental findings. In a recent comparative study, Allen (1980) points out that *gem*-dichloro substitution induces significant *distal*-bond lengthening in accord with theoretical predictions. An inverse but weaker phenomenon is observed for the *gem*-dichlorovinylcyclopropane unit of (1). The 'opposite' bond [C(1)—C(6) 1·507 (4) Å] is shorter than the two 'adjacent' bonds [C(1)—C(7) 1·523 (3); C(6)—C(7) 1·527 (4) Å]. This geometrical modification of the cyclopropane ring reveals the weak π-acceptor character of the dichlorovinyl substituent, as established for the vinyl group (Allen, 1980).

The less favourable *endo* configuration of the vinyl group results from mechanistic effects prevailing during the synthesis (Jefford *et al.*, 1982). The torsion about the C(7)—C(8) bond is due to intramolecular nonbonded interactions: H(8) is approximatively equally distant from H(5)*A* and H(2), at 2·79 (4) and 2·63 (4) Å respectively. Thus the vinyl group is almost perpendicular (82°) to the mean plane of the five-membered ring. This particular orientation is accompanied by a short contact distance between H(7) and Cl(4) [2·73 (3) Å] inducing a major opening of the C(7)—C(8)—C(9) bond angle and a slight torsion about the C(7)—C(8) bond [H(7)—C(7)—C(8)—H(8) = 160 (3)°] owing to the 'rigidity' of the adjoining olefinic bond. A value of 142° is suggested for this torsional angle, on the basis of the experimental ^{1}H NMR coupling constant $^3J_{\mathrm{H(7),H(8)}} = 7{\cdot}5$ Hz used in the Karplus equation derived for vinylcyclopropanes (Günther, Klose & Cremer, 1971). The agreement between both values is reasonable since ^3J also depends on the electronegativity of the neighbouring substituents (Trible & Traynham, 1972) and on the bond-angle variations (Günther, 1973). The *trans*-bisected conformation of the vinylcyclopropane moiety characterized by the value 162° for the torsional angle *X*1—C(6)—C(7)—C(8)* favours electron delocalization between the vinyl and cyclopropane groups (Hoffmann & Davidson, 1971). The occurrence of this interaction is supported by the short distance C(7)—C(8) [1·470 (4) Å] close to the mean value 1·465 (3) Å proposed by Allen (1980). The effect of the two Cl atoms on this bond appears to be negligible since the corresponding bond length in vinylcyclopropane is 1·475 Å (De Meijere & Lüttke, 1969).

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* *X*1 corresponds to the middle of the C(1)—C(6) bond (*cf.* Allen, 1980).

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