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(4*S*,7*R*)-7,8,8-Trimethyl-4,5,6,7-tetrahydro-4,7-methano-1*H*(2*H*)-indazole (Campho[2,3-*c*]pyrazole): Comparison Between the X-ray Structure and Carbon-13 NMR Data in the Solid State

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Abstract. $C_{11}H_{16}N_2$, $M_r = 176.26$, monoclinic, $P2_1$, $a = 13.4077$ (3), $b = 12.6064$ (3), $c = 19.0523$ (6) Å, $\beta = 98.392$ (2)°, $V = 3185.6$ (2) Å^3, $Z = 12$, $D_x = 1.102$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 4.777$ cm^{-1}, $F(000) = 1152$, $T = 295$ K, $R = 0.059$ for 5489 observed reflections. The six independent molecules in the asymmetric unit are associated into two trimers through quite linear N—H···N bonds. The ^{13}C NMR spectra (CP/MAS technique) of the title compound presents a sixfold multiplicity for most C atoms.

Introduction. We are currently carrying out a program of systematic exploration of pyrazole structures in order to understand the relationship between the pyrazole chemical formula and the molecular and crystal structure, with special emphasis on the hydrogen-bond network. Campho[2,3-*c*]pyrazole is one of the simplest and easiest chiral pyrazoles that can be prepared (Jacquier & Maury, 1967; Nagai, Oda, Ito & Kudo, 1979; Brunner & Scheck, 1992). This explains why this pyrazole and its *N*-substituted derivatives have been often used to prepare coordination complexes, searching for chiral homogeneous catalysts (Steel, 1983; Watson, House & Steel, 1986, 1989; House, Steel & Watson, 1986, 1987). Since the structure of the free ligand was not known and expecting that its chiral nature would induce some interesting features in the packing, we decided to study campho[2,3-*c*]pyrazole itself.

Experimental. Campho[2,3-*c*]pyrazole was prepared according to Jacquier & Maury (1967). M.p. 422 K, literature m.p. 416–417 K (Jacquier & Maury, 1967), 426–428 K (Nagai *et al.*, 1979). Suitable crystals for the X-ray analysis were obtained by slow evaporation of a saturated solution in diethyl ether–petroleum ether.

The crystal analysis parameters are presented in Table 1. After several unsuccessful attempts, the structure was solved by Patterson vector search rotation functions, *ORIENT*, followed by *DIRDIF* for the application of direct methods to difference structure factors (Beurskens *et al.*, 1984). A fragment, as the expected molecule (13 atoms), taken from a Pd complex retrieved from the Cambridge Structural Database [CSD hereinafter; refcode: DUZNUQ (Allen, Kennard & Taylor, 1983)] was used as a model. The absolute configuration, (+)-camphor, was not determined since it was known by synthesis; therefore, the final positional parameters for the non-H atoms shown in Table 2 display the same configuration as that established by Allen & Rogers (1971) and Bear & Trotter (1975) for (+)-3-bromocamphor and (+)-8-bromocamphor (CSD refcodes: BRCMPH10 and BCAMPH). 14 reflections suffered from secondary extinction and were omitted in the last cycles of refinement.

Atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).† Data processing and computations were carried out on a VAX 6410 computer using the

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† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55704 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1008]

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Table 1. *Crystal analysis parameters at room temperature*

Crystal data	
Crystal habit	Colourless cube
Crystal size (mm)	0.60 × 0.60 × 0.60
Unit-cell determination	Least-squares fit from 99 reflections ($\theta < 45°$)
Experimental data	
Diffractometer	Four-circle Philips PW1100, bisecting geometry
Radiation	Graphite-oriented-monochromated Cu $K\alpha$
Detector apertures (°)	1 × 1
Scan mode	$\omega/2\theta$
Scan width (°)	1.5
$+h$, $+k$, $\pm l$ range	15, 14, ±22
$\theta_{\max}$ (°)	65
Number of reflections:	
Measured	5938
Independent	5685
Observed [$3\sigma(I)$ criterion]	5489
R_{int}	0.015
Standard reflections:	
Number	2
Frequency (min)	90
Variation (%)	0
Solution and refinement	
Solution	Direct methods
Refinement	Least-squares on F_o; 8 blocks
Parameters:	
Number of variables	1087
Degrees of freedom	4402
Ratio of freedom	5.1
Goodness of fit	1.3
H-atom location	Difference synthesis
Final average shift/e.s.d.	0.09
Maximum shift/e.s.d.	0.42
Weighting scheme	Empirical so as to give no trends in $\langle w\Delta^2F\rangle$ *vs* $\langle \lvert F_o\rvert\rangle$ and $\langle \sin\theta/\lambda\rangle$
Maximum thermal value (Å^2)	U_{11}(C372) = 0.177 (8)
Final ΔF peaks (e Å^{-3})	±0.28
Final R, wR	0.059, 0.057

*XRAY*80 program package (Stewart *et al.*, 1976), *PESOS* (Martinez-Ripoll & Cano, 1975) and *PARST* (Nardelli, 1983).

The high-resolution ^{13}C CP/MAS NMR spectrum of a powdered sample of campho[2,3-*c*]pyrazole was recorded with TOSS sequence at 100.63 MHz, 5.5 μs 90° pulse width, 1 ms contact time and 6 s recycle delay, using a spectrometer (MSL 400, Bruker Karlsruhe, Germany) equipped with a Fourier transform unit. The spinning frequency at the magic angle (54.73°) was 4 kHz. The chemical shifts are expressed in p.p.m. from TMS. The spectrum is presented in Fig. 1.

Discussion. Tables 3 and 4 list selected bond lengths, bond angles, torsion angles and hydrogen-bond interactions. Fig. 2 presents an *ORTEP* drawing (Hall & Stewart, 1990) of one of the six independent molecules showing the numbering scheme.

The main differences among the molecules are mainly confined to the slightly different orientation of the pyrazole ring with the respect to the camphor moiety (torsion angles C*i*06—C*i*07—C*i*71—N*i*01, C*i*03—C*i*31—C*i*04—C*i*05 and N*i*01—C*i*71—C*i*07—C*i*08, Table 4).

The pyrazole ring, in the six independent molecules, presents a pattern of bonds and angles similar, to some extent, to that reported by Bonati (1989)

Table 2. *Final atomic coordinates and equivalent isotropic thermal parameters* (Å^2 × 10^4)

$$U_{\text{eq}} = (1/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j\cos(a_ia_j).$$

	x	y	z	U_{eq}
N101	−0.1452 (2)	0.1500†	0.5545 (1)	454 (7)
N102	−0.2221 (2)	0.2006 (2)	0.5119 (1)	488 (8)
C103	−0.3075 (2)	0.1430 (2)	0.5005 (2)	488 (8)
C131	−0.2884 (2)	0.0508 (2)	0.5372 (1)	465 (8)
C104	−0.3247 (2)	−0.0555 (3)	0.5596 (2)	550 (9)
C105	−0.2712 (3)	−0.1386 (3)	0.5200 (2)	626 (11)
C106	−0.1590 (3)	−0.1277 (3)	0.5522 (2)	622 (11)
C107	−0.1583 (2)	−0.0410 (2)	0.6100 (1)	484 (8)
C171	−0.1873 (2)	0.0588 (2)	0.5690 (1)	416 (7)
C172	−0.0644 (3)	−0.0371 (4)	0.6651 (2)	655 (12)
C108	−0.2625 (2)	−0.0625 (3)	0.6364 (2)	547 (9)
C181	−0.2691 (4)	−0.1711 (4)	0.6712 (3)	816 (16)
C182	−0.2914 (3)	0.0219 (5)	0.6869 (2)	772 (15)
N301	0.0101 (2)	0.3924 (2)	0.6127 (1)	547 (8)
N302	−0.0098 (2)	0.2974 (2)	0.6409 (1)	505 (7)
C303	0.0318 (3)	0.2884 (3)	0.7093 (2)	646 (11)
C331	0.0822 (2)	0.3808 (2)	0.7270 (1)	508 (8)
C304	0.1555 (3)	0.4439 (3)	0.7787 (2)	697 (12)
C305	0.2571 (3)	0.4378 (6)	0.7488 (4)	1212 (27)
C306	0.2369 (3)	0.5036 (7)	0.6812 (3)	1209 (28)
C307	0.1252 (2)	0.5440 (3)	0.6769 (1)	593 (10)
C371	0.0677 (2)	0.4417 (2)	0.6656 (1)	446 (8)
C372	0.0930 (8)	0.6335 (6)	0.6277 (3)	1250 (32)
C308	0.1224 (2)	0.5578 (2)	0.7579 (1)	482 (8)
C381	0.1952 (4)	0.6423 (4)	0.7939 (2)	730 (15)
C382	0.0165 (3)	0.5858 (4)	0.7729 (3)	826 (17)
N501	−0.1806 (2)	0.4058 (2)	0.4522 (1)	490 (7)
N502	−0.1132 (2)	0.4776 (2)	0.4853 (1)	521 (8)
C503	−0.1168 (3)	0.5719 (3)	0.4515 (2)	595 (10)
C531	−0.1898 (2)	0.5631 (2)	0.3938 (1)	486 (8)
C504	−0.2457 (3)	0.6102 (3)	0.3269 (2)	581 (10)
C505	−0.2020 (3)	0.5543 (4)	0.2658 (2)	713 (13)
C506	−0.2389 (3)	0.4398 (3)	0.2702 (2)	721 (13)
C507	−0.3028 (2)	0.4401 (2)	0.3327 (2)	525 (9)
C571	−0.2256 (2)	0.4599 (2)	0.3968 (1)	421 (7)
C572	−0.3733 (5)	0.3482 (5)	0.3359 (4)	968 (20)
C508	−0.3488 (2)	0.5545 (3)	0.3245 (2)	520 (9)
C581	−0.4200 (3)	0.5723 (5)	0.2542 (2)	785 (16)
C582	−0.4038 (4)	0.5865 (5)	0.3855 (2)	775 (15)
N201	−0.3687 (2)	0.7020 (2)	−0.0410 (1)	479 (7)
N202	−0.2861 (2)	0.6795 (2)	0.0077 (1)	460 (7)
C203	−0.2936 (2)	0.7220 (3)	0.0725 (1)	530 (9)
C231	−0.3854 (2)	0.7710 (2)	0.0666 (1)	465 (8)
C204	−0.4564 (2)	0.8424 (3)	0.0982 (2)	563 (9)
C205	−0.4467 (3)	0.9528 (3)	0.0627 (3)	786 (14)
C206	−0.4906 (3)	0.9339 (3)	−0.0148 (2)	768 (14)
C207	−0.5256 (2)	0.8162 (3)	−0.0179 (2)	552 (9)
C271	−0.4270 (2)	0.7567 (2)	−0.0042 (1)	423 (7)
C272	−0.5999 (3)	0.7821 (5)	−0.0820 (2)	960 (18)
C208	−0.5591 (2)	0.8035 (3)	0.0572 (2)	542 (9)
C281	−0.6491 (3)	0.8749 (4)	0.0679 (3)	799 (14)
C282	−0.5831 (3)	0.6907 (4)	0.0770 (3)	817 (15)
N401	−0.3117 (2)	0.5683 (2)	−0.2085 (1)	467 (7)
N402	−0.3850 (2)	0.6310 (2)	−0.1878 (1)	498 (7)
C403	−0.4697 (2)	0.6333 (2)	−0.2370 (1)	502 (8)
C431	−0.4509 (2)	0.5722 (2)	−0.2923 (1)	407 (7)
C404	−0.4863 (2)	0.5255 (2)	−0.3640 (1)	442 (7)
C405	−0.4239 (3)	0.5822 (3)	−0.4153 (2)	583 (10)
C406	−0.3157 (2)	0.5396 (3)	−0.3921 (2)	590 (10)
C407	−0.3253 (2)	0.4631 (2)	−0.3293 (1)	435 (7)
C471	−0.3524 (2)	0.5345 (2)	−0.2716 (1)	391 (7)
C472	−0.2393 (2)	0.3866 (3)	−0.3105 (2)	704 (12)
C408	−0.4329 (2)	0.4157 (2)	−0.3549 (1)	407 (7)
C481	−0.4404 (3)	0.3507 (3)	−0.4236 (2)	626 (11)
C482	−0.4724 (3)	0.3459 (3)	−0.2985 (2)	607 (10)
N601	−0.1228 (2)	0.5570 (2)	−0.0407 (1)	459 (7)
N602	−0.1429 (2)	0.5037 (2)	−0.1034 (1)	452 (7)
C603	−0.0795 (2)	0.4213 (3)	−0.1072 (2)	579 (10)
C631	−0.0154 (2)	0.4190 (3)	−0.0450 (1)	529 (9)
C604	0.0744 (3)	0.3704 (4)	0.0009 (2)	715 (12)
C605	0.1601 (3)	0.4505 (6)	0.0008 (2)	922 (19)
C606	0.1264 (3)	0.5447 (5)	0.0423 (3)	837 (17)
C607	0.0240 (2)	0.5121 (3)	0.0636 (1)	536 (9)
C671	−0.0451 (2)	0.5049 (2)	−0.0064 (1)	417 (7)
C672	−0.0131 (5)	0.5756 (6)	0.1215 (2)	998 (22)
C608	0.0427 (3)	0.3891 (3)	0.0754 (2)	656 (11)
C681	0.1281 (5)	0.3627 (5)	0.1361 (2)	1019 (21)
C682	−0.0505 (5)	0.3270 (6)	0.0868 (4)	1067 (24)

† Coordinate fixed to define origin of structure with non-centrosymmetric space group.

Table 3. *Selected bond distances* (Å) *and bond angles* (°)

	i = 1	*i* = 3	*i* = 5	*i* = 2	*i* = 4	*i* = 6
N*i*01—N*i*02	1.373 (3)	1.355 (4)	1.366 (4)	1.367 (3)	1.363 (4)	1.363 (3)
N*i*01—C*i*71	1.328 (3)	1.326 (4)	1.326 (3)	1.318 (4)	1.317 (3)	1.320 (3)
N*i*02—C*i*03	1.347 (4)	1.345 (4)	1.350 (5)	1.364 (4)	1.362 (4)	1.350 (4)
C*i*03—C*i*31	1.362 (4)	1.364 (5)	1.364 (4)	1.366 (4)	1.358 (4)	1.360 (4)
C*i*31—C*i*04	1.508 (5)	1.512 (5)	1.504 (4)	1.499 (5)	1.499 (4)	1.511 (5)
C*i*31—C*i*71	1.406 (3)	1.389 (4)	1.392 (4)	1.395 (4)	1.405 (3)	1.399 (4)
C*i*04—C*i*05	1.531 (5)	1.553 (7)	1.547 (5)	1.561 (5)	1.551 (4)	1.531 (7)
C*i*04—C*i*08	1.577 (4)	1.537 (5)	1.546 (5)	1.559 (4)	1.557 (4)	1.559 (5)
C*i*05—C*i*06	1.547 (5)	1.522 (11)	1.531 (7)	1.526 (7)	1.550 (5)	1.532 (9)
C*i*06—C*i*07	1.550 (5)	1.573 (6)	1.566 (5)	1.555 (5)	1.557 (5)	1.543 (6)
C*i*07—C*i*71	1.501 (4)	1.508 (5)	1.502 (4)	1.509 (4)	1.507 (4)	1.512 (4)
C*i*07—C*i*72	1.519 (5)	1.490 (8)	1.502 (7)	1.522 (5)	1.507 (5)	1.506 (7)
C*i*07—C*i*08	1.576 (4)	1.560 (4)	1.568 (4)	1.569 (5)	1.572 (3)	1.582 (5)
C*i*08—C*i*81	1.529 (6)	1.537 (6)	1.543 (5)	1.543 (5)	1.535 (4)	1.540 (6)
C*i*08—C*i*82	1.523 (6)	1.529 (6)	1.518 (6)	1.517 (6)	1.540 (5)	1.516 (9)
N*i*02—N*i*01—C*i*71	102.7 (2)	103.6 (2)	102.7 (2)	103.4 (2)	103.3 (2)	103.3 (2)
N*i*01—N*i*02—C*i*03	113.1 (2)	112.5 (3)	112.8 (3)	111.9 (2)	112.2 (2)	112.4 (2)
N*i*02—C*i*03—C*i*31	106.6 (3)	106.7 (3)	106.5 (3)	106.7 (2)	106.9 (3)	107.0 (3)
C*i*03—C*i*31—C*i*71	104.9 (3)	104.8 (3)	104.7 (3)	104.5 (3)	104.3 (2)	104.4 (3)
C*i*03—C*i*31—C*i*04	149.3 (3)	149.6 (3)	149.4 (3)	148.8 (3)	149.3 (3)	149.6 (3).
C*i*04—C*i*31—C*i*71	105.8 (2)	105.1 (3)	105.7 (2)	106.2 (2)	106.4 (2)	105.9 (3)
C*i*31—C*i*04—C*i*08	99.4 (2)	100.9 (3)	100.3 (3)	100.2 (3)	99.7 (2)	99.5 (3)
C*i*31—C*i*04—C*i*05	105.9 (3)	104.9 (4)	105.2 (3)	105.3 (3)	105.4 (2)	105.5 (4)
C*i*05—C*i*04—C*i*08	101.3 (3)	100.8 (4)	101.9 (3)	100.8 (3)	101.5 (2)	101.9 (3)
C*i*04—C*i*05—C*i*06	104.0 (3)	103.0 (4)	103.2 (3)	103.6 (3)	103.3 (2)	103.5 (3)
C*i*05—C*i*06—C*i*07	104.4 (3)	105.8 (4)	104.8 (3)	104.9 (3)	104.7 (2)	105.7 (4)
C*i*06—C*i*07—C*i*08	101.1 (3)	98.3 (3)	100.3 (3)	100.8 (3)	100.0 (2)	99.8 (3)
C*i*06—C*i*07—C*i*72	115.6 (3)	117.7 (4)	116.5 (3)	117.3 (3)	115.7 (2)	117.0 (4)
C*i*06—C*i*07—C*i*71	104.3 (2)	101.7 (4)	103.3 (3)	102.5 (3)	104.3 (2)	103.8 (3)
C*i*72—C*i*07—C*i*08	118.0 (3)	119.4 (4)	118.2 (3)	117.6 (3)	117.8 (3)	118.6 (3)
C*i*71—C*i*07—C*i*08	97.8 (2)	98.6 (3)	98.2 (2)	98.8 (2)	98.4 (2)	97.5 (2)
C*i*71—C*i*07—C*i*72	117.3 (3)	117.5 (4)	117.2 (3)	116.9 (3)	117.8 (3)	116.9 (2)
C*i*31—C*i*71—C*i*07	108.9 (2)	110.0 (2)	108.8 (2)	108.6 (2)	108.3 (2)	108.9 (3)
N*i*01—C*i*71—C*i*07	138.5 (2)	137.5 (3)	137.9 (3)	137.8 (3)	138.5 (2)	138.2 (3)
N*i*01—C*i*71—C*i*31	112.6 (2)	112.4 (3)	113.2 (2)	113.4 (2)	113.2 (2)	112.9 (2)
C*i*04—C*i*08—C*i*07	93.9 (2)	95.9 (2)	94.4 (2)	94.3 (2)	94.7 (2)	94.4 (3)
C*i*07—C*i*08—C*i*82	113.6 (3)	111.6 (3)	113.3 (3)	115.0 (3)	113.3 (2)	114.2 (4)
C*i*07—C*i*08—C*i*81	113.7 (3)	114.4 (3)	113.8 (3)	113.2 (3)	114.2 (2)	113.8 (4)
C*i*04—C*i*08—C*i*82	113.5 (4)	114.1 (3)	112.9 (3)	112.0 (3)	112.8 (2)	113.1 (4)
C*i*04—C*i*08—C*i*81	113.4 (4)	113.1 (3)	113.4 (3)	113.6 (3)	114.1 (2)	112.3 (4)
C*i*81—C*i*08—C*i*82	108.4 (3)	107.6 (3)	108.6 (3)	108.4 (3)	107.7 (3)	108.6 (4)

Table 4. *Selected torsion angles* (°) *and hydrogen-bonding geometry* (Å, °)

	i = 1	*i* = 3	*i* = 5	*i* = 2	*i* = 4	*i* = 6
C*i*03—C*i*31—C*i*04—C*i*05	109.1 (5)	98.8 (7)	103.2 (6)	99.6 (6)	111.2 (5)	105.9 (6)
C*i*03—C*i*31—C*i*04—C*i*08	−146.2 (5)	−156.8 (6)	−151.3 (5)	−156.1 (5)	−143.9 (5)	−148.8 (6)
C*i*04—C*i*31—C*i*71—C*i*07	1.0 (3)	−1.8 (3)	0.4 (3)	−1.4 (3)	−0.6 (3)	−0.1 (3)
C*i*71—C*i*31—C*i*04—C*i*08	34.1 (3)	34.2 (3)	34.0 (3)	35.1 (3)	34.7 (3)	34.9 (3)
C*i*71—C*i*31—C*i*04—C*i*05	−70.7 (3)	−70.2 (4)	−71.4 (3)	−69.2 (3)	−70.2 (3)	−70.3 (4)
C*i*31—C*i*04—C*i*08—C*i*82	64.8 (3)	65.8 (4)	65.5 (4)	66.9 (3)	65.2 (3)	65.5 (4)
C*i*31—C*i*04—C*i*08—C*i*07	−53.0 (3)	−51.0 (3)	−52.2 (3)	−52.2 (3)	−52.4 (2)	−53.2 (3)
C*i*31—C*i*04—C*i*05—C*i*06	66.7 (3)	68.8 (5)	67.9 (3)	67.1 (4)	68.6 (3)	68.2 (4)
C*i*04—C*i*05—C*i*06—C*i*07	1.9 (3)	0.4 (6)	1.2 (4)	1.8 (4)	−0.4 (3)	0.2 (5)
C*i*05—C*i*06—C*i*07—C*i*71	−67.7 (3)	−66.5 (5)	−67.5 (3)	−68.2 (3)	−66.3 (3)	−66.2 (4)
C*i*05—C*i*06—C*i*07—C*i*72	162.1 (3)	163.7 (5)	162.5 (4)	162.3 (4)	162.7 (3)	163.4 (4)
C*i*05—C*i*06—C*i*07—C*i*08	33.5 (3)	34.1 (5)	33.6 (3)	33.4 (4)	35.1 (3)	34.2 (4)
C*i*06—C*i*07—C*i*71—C*i*31	68.2 (3)	69.8 (4)	68.8 (3)	70.7 (3)	69.5 (3)	68.2 (3)
C*i*08—C*i*07—C*i*71—C*i*31	−35.5 (3)	−30.5 (3)	−33.9 (3)	−32.5 (3)	−33.2 (3)	−33.9 (3)
C*i*08—C*i*07—C*i*71—N*i*01	144.9 (3)	154.4 (3)	149.7 (3)	152.6 (3)	144.8 (3)	147.4 (4)
C*i*06—C*i*07—C*i*71—N*i*01	−111.6 (4)	−105.2 (4)	−107.6 (4)	−104.2 (4)	−112.6 (4)	−110.5 (4)
C*i*06—C*i*07—C*i*08—C*i*04	−53.8 (3)	−54.8 (3)	−53.9 (3)	−54.2 (3)	−55.0 (2)	−53.6 (3)
C*i*72—C*i*07—C*i*08—C*i*04	179.2 (3)	176.8 (4)	178.3 (4)	177.1 (3)	178.8 (4)	178.2 (4)
C*i*71—C*i*07—C*i*08—C*i*04	52.6 (2)	48.4 (3)	51.3 (3)	50.4 (3)	51.2 (2)	51.9 (3)
C*i*06—C*i*07—C*i*08—C*i*81	63.9 (4)	63.9 (4)	64.0 (4)	63.8 (4)	64.0 (3)	63.2 (4)
C*i*72—C*i*07—C*i*71—N*i*01	17.7 (5)	24.7 (6)	22.0 (6)	25.5 (5)	17.2 (5)	19.9 (6)
C*i*72—C*i*07—C*i*08—C*i*81	−63.1 (4)	−64.6 (5)	−63.8 (5)	−65.0 (4)	−62.2 (3)	−65.0 (5)
C*i*72—C*i*07—C*i*08—C*i*82	61.5 (4)	57.9 (5)	61.0 (5)	60.4 (4)	61.6 (3)	60.5 (5)
C*i*71—C*i*07—C*i*08—C*i*82	−65.1 (3)	−70.4 (3)	−66.0 (3)	−66.3 (3)	−66.0 (3)	−65.8 (4)

N602···N401···N402···N201	1.41 (25)	N102···N501···N502···N301	9.15 (26)
N401···N402···N201···N202	3.87 (30)	N501···N502···N301···N302	−9.67 (31)
N402···N201···N202···N601	0.40 (25)	N502···N301···N302···N101	15.67 (28)
N201···N202···N601···N602	−16.27 (28)	N301···N302···N101···N102	−35.79 (27)
N202···N601···N602···N401	21.83 (24)	N302···N101···N102···N501	34.94 (21)
N601···N602···N401···N402	−17.64 (28)	N101···N102···N501···N502	−32.01 (30)

N—H···N	N···N	N—H	N···N	N—H···N
N102—H102···N501	2.911 (4)	0.69 (6)	2.22 (6)	177 (5)
N302—H302···N101	2.931 (3)	0.72 (5)	2.22 (4)	171 (5)
N502—H502···N301	2.933 (3)	0.76 (4)	2.18 (4)	173 (5)
N202—H202···N601	2.936 (3)	0.80 (4)	2.14 (4)	178 (3)
N402—H402···N201	2.914 (3)	0.82 (4)	2.10 (4)	170 (3)
N602—H602···N401	2.910 (3)	0.81 (4)	2.10 (4)	179 (5)

for pyrazoles with substituents on positions 3, 4 and 5 of the ring (1.364, 1.356, 1.379, 1.403 and 1.331 Å for N1—N2, N2—C3... bonds and 105.0, 111.6, 106.6, 105.4 and 111.3° for angles at N1, N2... respectively). The differences arise from the lengthening of the N*i*01—N*i*02 bond and the shortening of the N*i*02—C*i*03 and C*i*03—C*i*31 bonds (Table 3).

The main peculiarity of the solid-state structure is the formation of two trimers *via* N—H···N hydrogen bonds (Table 4 and Fig 3). These interactions are stronger and more linear than the mean interactions found in organic crystals for N—H···Nsp^2 bonds retrieved from the CSD where the acceptor was bonded to N and C atoms as in the pyrazole moiety [N···N = 2.971 Å and N—H···N = 161° (Llamas-Saiz & Foces-Foces, 1990)].

The central six-membered rings, H atoms excluded, adopt a distorted half-chair toward an envelope conformation and a slightly distorted 1,3-diplanar conformation for the $i = 1, 3, 5$ and $i = 2, 4, 6$ molecules respectively [Cremer & Pople (1975) parameters for $i = 1, 3, 5$: $Q_2 = 0.238\,(3)$, $Q_3 = 0.267\,(2)$ Å, $\varphi_2 = 77.1\,(7)$, $\theta_2 = 41.7\,(4)$°; and for $i =$

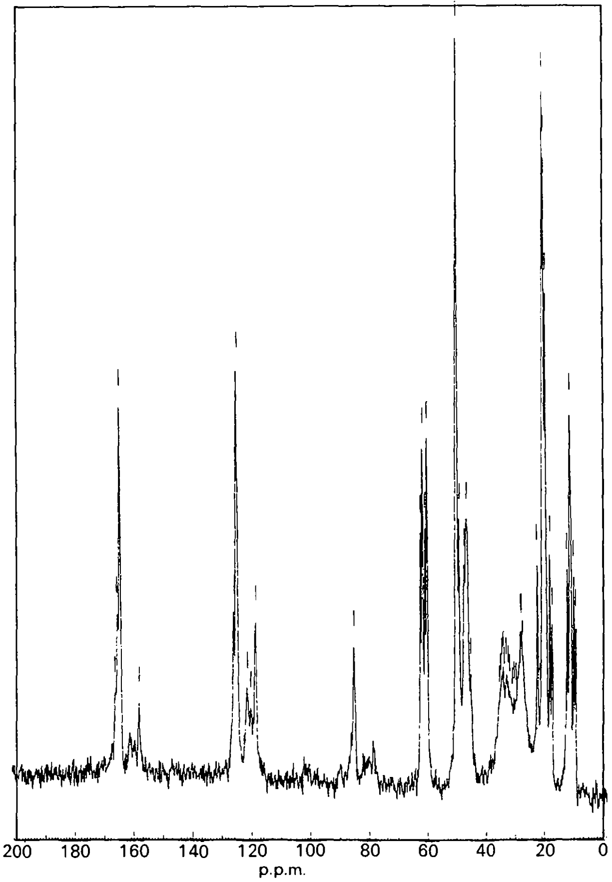

Fig. 1. High-resolution CP/MAS ^{13}C NMR spectrum of campho-[2,3-*c*]pyrazole.

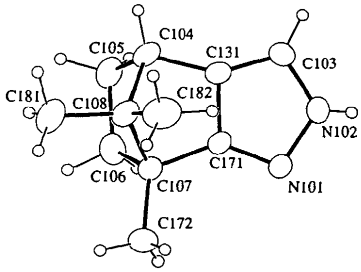

Fig. 2. View of molecule 1 showing the numbering scheme. Thermal ellipsoids are drawn at 30% probability level and H atoms are represented by spheres of 0.1 Å radii.

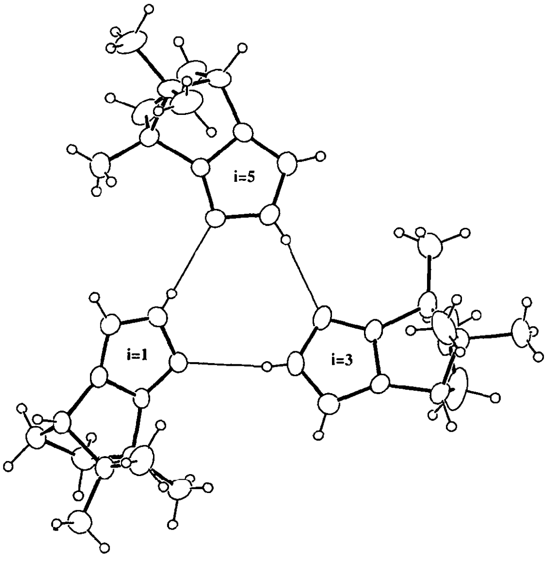

Fig. 3. A perspective view of one trimeric association.

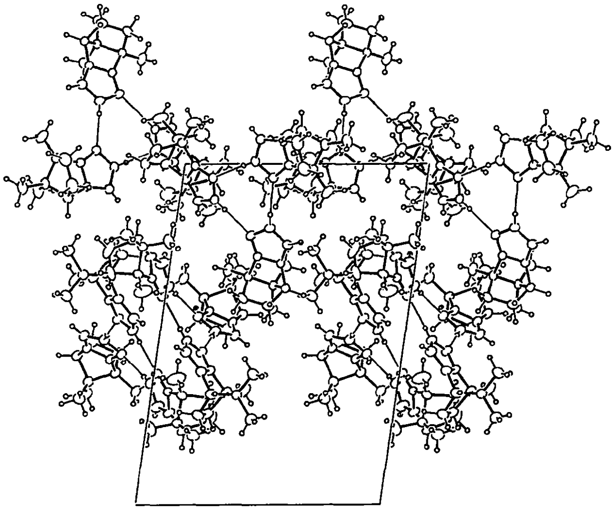

Fig. 4. The packing diagram as projected along the *b* axis.

Table 5. ^{13}C *NMR chemical shifts of campho*[2,3-*c*]*pyrazole*

Carbons	C*i*03	C*i*31	C*i*04	C*i*05	C*i*06	C*i*07	C*i*71	Me*i*72	C*i*08	Me*i*81	Me*i*82
	1	2	3	4	5	6	7	8	9	10	11
Molecule											
a	118.31	124.94	45.39	27.72	32.22	60.41	164.84	9.62	49.24	17.59	20.29
b	118.31	124.94	46.77	28.18	33.20	60.41	164.84	10.29	49.99	18.29	20.29
c	118.31	124.94	46.77	28.47	33.99	61.04	164.84	11.58	49.99	19.68	20.73
d	120.12	124.94	46.77	30.06	34.35	61.81	164.84	11.58	49.99	19.68	20.73
e	121.32	125.78	47.52	30.66	34.73	61.81	165.74	11.58	49.99	20.29	21.81
f	121.32	125.78	47.52	31.20	35.63	62.46	166.32	12.49	49.99	20.29	22.88

2, 4, 6: $Q_2 = 0.195\,(3)$, $Q_3 = 0.103\,(3)$ Å, $\varphi_2 = 92.1\,(8)$, $\theta_2 = 62.1\,(7)°$]. A similar trimeric disposition has been previously observed in 3-phenyl-4-bromopyrazole (Aguilar *et al.*, 1992) [$q_2 = 0.280\,(5)$, $q_3 = 0.173\,(5)$ Å, $\varphi_2 = 93.6\,(11)$ and $\theta_2 = 57.8\,(10)°$] and 3,5-dimethylpyrazole (planar central ring) (Smith *et al.*, 1989).

The crystal is built of sheets of trimers parallel to the *c* axis, molecules *i* = 1, 3, 5 alternating with *i* = 2, 4, 6 (Fig. 4). No interactions between sheets have been detected.

All the comparisons (15 pairs) between the six independent molecules in the asymmetric unit have been performed by means of a least-squares technique based on the atomic coordinates (Nardelli, 1983) and by statistical methods (Abrahams & Keve, 1971) using distances up to 4.0 Å. The minor differences are presented by the following pairs of molecules: 5–6, 1–6, 4–6, 1–4, 2–3 and 2–5; the major ones are presented by 1–2 and 1–3.

The only previously reported campho[2,3-*c*]-pyrazole, which acts as a ligand in a Cu complex [CSD refcode: JEZGAW (Watson *et al.*, 1989)], reveals that its greatest similarity is with molecule 1.

The ^{13}C NMR spectrum (Fig. 1) can be decomposed into a sum of six spectra (Table 5). The assignment was made by analogy with the values in solution (Watson *et al.*, 1989). Although the resolution was exceptionally good, some signals are superimposed; in this case, the intensity of the signals was taken into account to determine how many C atoms have the same chemical shift. The chemical shifts of C atoms C*i*03 and C*i*71 are consistent only with 2*H*-tautomers, in agreement with the X-ray structure (all the six molecules have the proton at position 2) and with the results in solution (Watson *et al.*, 1989). The reason why this tautomer is favoured over the 1*H* is probably related to angular strains in the ring fusion {campho[2,3-*c*]pyrazole is a weaker base than expected (Elguero, Gonzalez & Jacquier, 1968)}.

Although the assignment of the set of signals to the corresponding C atoms (for instance, 118.31–121.32 to C*i*03) presents no particular difficulty when the assignment in solution is known, the problem of attributing each one to a given molecule of the crystal is a very difficult one. As a matter of fact, the individuality of geometries characteristic of the X-ray structures is no longer maintained in NMR; for the moment, to connect the ^{13}C chemical shifts of a given molecule in ^{13}C CP/MAS using 2*D*-spin diffusion (Szeverinyi, Sullivan & Maciel, 1982; Limbach, Wehrle, Zimmermann, Kendrick & Yannoni, 1987) needs an enrichment by a factor of 10 to make this a feasible experiment. Thus, the assignment in Table 5 (from low to high field for each C atom) is arbitrary.

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Acta Cryst. (1993). C**49**, 729–731

Structure of (4*α*)-13-Hydroxykaur-16-en-18-oic Acid (Steviol) Methanol Solvate

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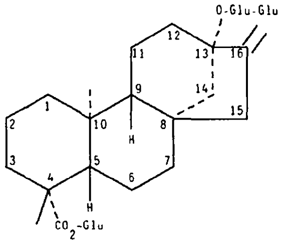
Abstract. $C_{20}H_{30}O_3.CH_4O$, $M_r = 350.50$, orthorhombic, $P2_12_12_1$, $a = 7.407\,(2)$, $b = 14.442\,(3)$, $c = 17.696\,(3)$ Å, $V = 1893\,(1)$ Å^3, $Z = 4$, D_m(flotation) = 1.20 g cm^{-3}, $D_x = 1.230$ g cm^{-3}, λ(Cu $K\alpha$) = 1.54056 Å, $\mu = 6.3$ cm^{-1}, $F(000) = 768$, $T = 298\,(1)$ K, final $R = 0.058$ for 1675 observed reflections. The hydrogen-bonding scheme consists of head-to-tail associated steviol molecules forming a ribbon in the **a** direction. The methanol molecule is hydrogen bonded to the carbonyl of the carboxyl group (acceptor) and to the hydroxyl group (donor) of associated steviol molecules.

Introduction. As a result of the banning of cyclamate for use as a non-nutritive sweetener and of the question raised regarding the possible carcinogenicity of saccharin, a great deal of work has been carried out recently directed toward the development of alternative sweeteners.

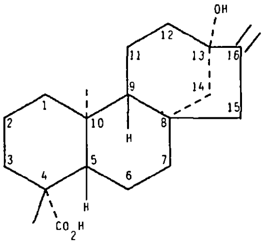
Stevioside (I), the extremely sweet diterpenoid glycoside found in the South American shrub *Stevia rebaudiana*, has been valued as a sweetener by the indigenous population. More recently, the plant source has been cultivated quite intensively in Japan where the product is approved for use in food.

Enzymatic hydrolysis of the diterpenoid glycoside stevioside by the gastric juices of the snail, *Helix pomatia* (Bridel & Lavieille, 1931), pectinase (Ruddat, Heftmann & Lang, 1965) or hesperidinase (Mizukami, Shiba & Ohashi, 1982), affords the aglycone steviol (II). Studies of the sweeteners of stevioside analogue compounds suggest that all of the functionality involved in receptor binding is located in the aglycon diterpenoid (Dubois, Dietrich, Lee, McGarraugh & Stephenson, 1981).

The differences in the structural features of diterpenes have an important role in their biological activity. Thus the following structure determination was undertaken.



(I)



(II)

Experimental. Colorless crystals of the title compound were prepared by Dr Mauro Alvarez (Departamento de Farmácia e Bioquímica, Universidade Estadual de Maringá).

A crystal of dimensions 0.75 × 0.25 × 0.20 mm was used for data collection. Cell dimensions were refined by a least-squares fit to the setting angles of 25 reflections ($7 < \theta < 12°$) on a CAD-4 automatic diffractometer. Intensity measurements were carried out up to 68° in θ with graphite-monochromated Cu $K\alpha$ radiation and employing the ω–2θ scan technique. Reflections were collected in the range 0 to 8 for h, 0 to 17 for k and 0 to 21 for l. Lorentz and polarization corrections were applied but no absorption correction was made. Two standard reflections