*SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: CF1072). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dicyano(7,7-dimethyl-2,5-di-*p*-tolyl-3,4-diazabicyclo[4.1.0]hepta-2,4-dien-3-ium-3-yl)methanide and (4-Benzoyl-5,5-dimethyl-2-phenyl-1-azacyclopenta-1,3-dien-1-ium-1-yl)dicyanomethanide, Two Stable Azomethine Ylides

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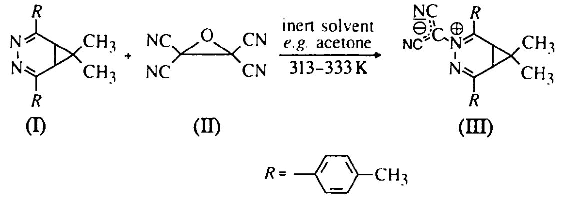
Abstract

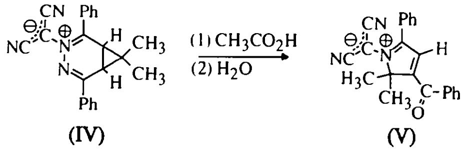
The azomethine ylide moieties of dicyano(7,7-dimethyl-2,5-di-*p*-tolyl-3,4-diazabicyclo[4.1.0]hepta-2,4-dien-3-ium-3-yl)methanide, $C_{24}H_{22}N_4$, and (4-benzoyl-5,5-dimethyl-2-phenyl-1-azacyclopenta-1,3-dien-1-ium-1-yl)dicyanomethanide, $C_{22}H_{17}N_3O$, show normal bond distances and angles in comparison with related structures reported previously. The dipolar N—C distances of 1.430 (4) and 1.401 (3) Å are appreciably shortened compared with the C—N$^+$ bond lengths [1.485 (9) Å] found in *N*-substituted pyridinium compounds, which is consistent with previous observations. Both title compounds pack in such a way that the ylide dipoles are arranged above each other but pointing in opposite directions.

Comment

3,4-Diazanorcaradienes, (I), show high reactivity in Diels–Alder reactions with inverse electron demand (Sauer, 1992, 1994). In order to lower the LUMO (lowest unoccupied molecular orbital) energy of these diazadienes, the introduction of a substituent at the N atom of the diene system was attempted. Reaction of diazanorcaradiene (I) with tetracyanoethylene oxide, (II), yielded the stable betaine (III) (Riebel, Weber, Troll, Sauer & Breu, 1996).



These betaines, which are also cationic 2,3-diazadienes and azomethine ylides, underwent a facile and unexpected rearrangement to form another stable betaine, (V), as shown for the reaction of the diphenyl derivative (IV) to (V). In compound (V), the combination of a cyclic azadiene and a 1,3-dipole is again found (Riebel, Weber, Troll, Sauer, Breu & Nöth, 1996). In order to characterize this reaction unambiguously, the X-ray structure determinations of compounds (III) and (V) were undertaken.



The molecular structures of (III) and (V) are represented in Figs. 1 and 2, respectively. There is only one diazanorcaradiene structure (Krieger, Fritchie & Blumburg, 1969) deposited in the Cambridge Structural Database (Allen *et al.*, 1987), however, crystal decomposition prevented an accurate determination of the molecular parameters and no coordinates were reported. Whereas for 2,5-di-*p*-bromophenyl-1,6-diphenyl-

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endo-7-phenyl-3,4-diazanorcaradiene, the six-membered heterocyclic ring was found to be nearly planar, with a maximum deviation of 0.07 Å, in compound (III), the heterocyclic ring is clearly not planar. Atoms C15 and C16 deviate by 0.352 (7) and 0.389 (7) Å, respectively, from the 2,3-diazadiene plane. The cyclopropyl group is tilted by 74.2 (2)° with respect to the best plane through the six-membered heterocyclic ring. The tolyl groups are twisted by 38.3 (2) (C21–C26) and 57.9 (2)° (C31–C36), and the dicyanomethanide group by 23.7 (2)°, with respect to the 2,3-diazadiene plane.

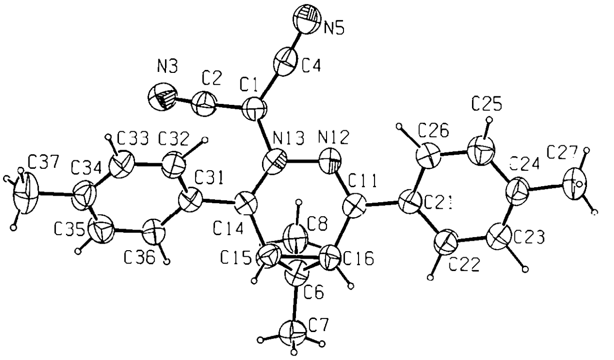

Fig. 1. The molecular structure of compound (III) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

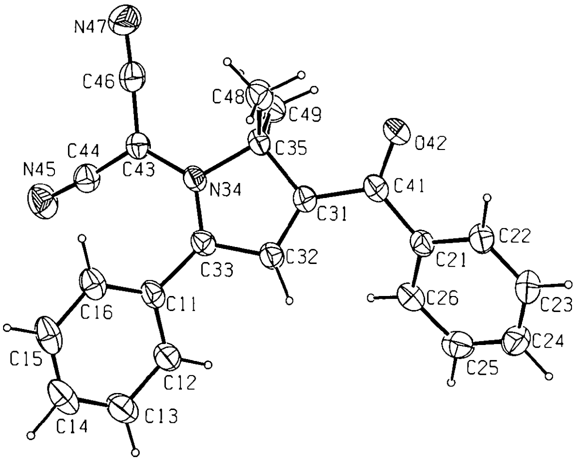

Fig. 2. The molecular structure of compound (V) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

The C14—N13 and C33—N34 bond lengths of 1.319 (5) and 1.331 (3) Å in compounds (III) and (V), respectively, are normal, indicating no conjugation of the negative charge onto atoms C14 or C33. The azomethine ylide moieties of both compounds show normal bond distances and angles compared with related structures deposited in the Cambridge Structural Database (Allen *et al.*, 1987). As noted previously (Matsubayashi, Sakamoto, Tanaka & Nakatsu, 1985), the N13—C1 and N34—C43 distances [1.430 (5) and 1.401 (3) Å, respectively] are appreciably shortened compared with the C—N^+ bond lengths found in *N*-substituted pyridinium com-

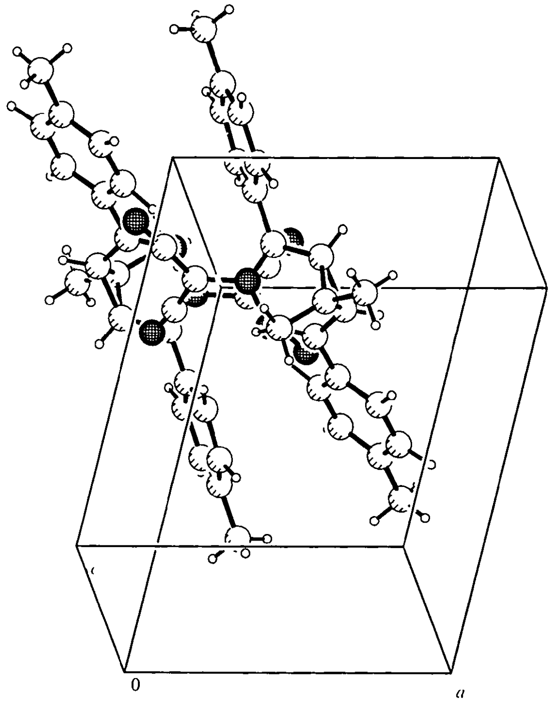

Fig. 3. The molecular packing of compound (III) showing the arrangement of the ylide dipoles.

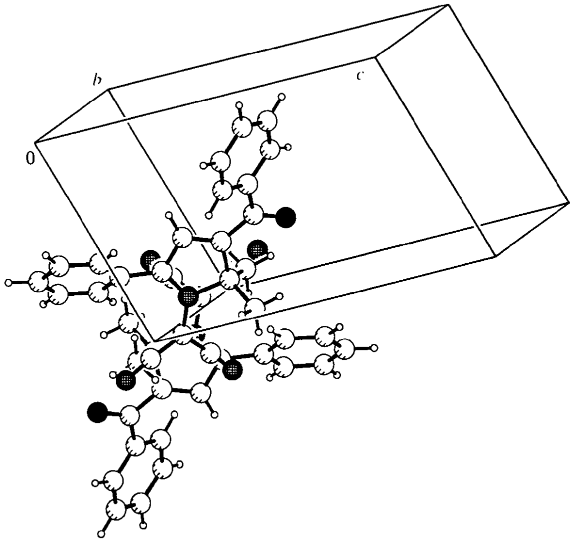

Fig. 4. The molecular packing of compound (V) showing the arrangement of the ylide dipoles.

pounds (1.485 Å; Wilson, 1995). Though not significant within a 3σ limit, the cyanide bonds are consistently longer than the mean bond length reported (1.136 Å; Wilson, 1995).

The azacyclopentadiene ring in compound (V) is planar; the maximum deviations from the least-squares plane are 0.020 (9) for C35 and 0.020 (9) Å for N34. Again, neither the dicyanomethanide nor the phenyl (C11–C15) groups are coplanar with the azadiene system, the dihedral angles between the best planes being 27.54 (9) and 37.39 (8)°, respectively. The carbonyl group is neither conjugated with the azadiene moiety nor with the adjacent phenyl group; torsion angles C32—C31—C41—O42 and C22—C21—C41—O42 are −163.7 (2) and 30.1 (3)°, respectively.

For both compounds (III) and (V), the molecules pack in such a way as to arrange the ylide dipoles above each other, but pointing in opposite directions (Figs. 3 and 4). The dipole distances N13—C1^{i}/C1—N13^{i} and N34—C43^{ii}/C43—N34^{ii} are 4.519 (6) and 4.740 (4) Å, respectively [symmetry codes: (i) $-x$, $2-y$, $-z$; (ii) $2-x$, $1-y$, $-z$].

Experimental

The reaction of diazanorcaradiene (I) with tetracyanoethylene oxide, (II), through gentle warming in an inert solvent, *e.g.* acetone, yielded the stable orange–red betaine (III) in 87% yield (Riebel, Weber, Troll, Sauer & Breu, 1996). The diphenyl derivative of compound (III), *i.e.* (IV), underwent a facile and unexpected rearrangement by gentle warming in acetic or formic acid to form another stable betaine, (V), in 42% yield.

Compound (III)

Crystal data

$C_{24}H_{22}N_4$
M_r = 366.47
Triclinic
$P\overline{1}$
a = 9.3641 (11) Å
b = 10.4565 (14) Å
c = 11.3107 (15) Å
α = 71.471 (10)°
β = 76.131 (10)°
γ = 75.272 (10)°
V = 1000.2 (3) Å^3
Z = 2
D_x = 1.217 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 1258 reflections
θ = 1.93–24.20°
μ = 0.07 mm^{-1}
T = 170 (2) K
Needle
0.30 × 0.06 × 0.05 mm
Orange–red

Data collection

Stoe IPDS diffractometer
Rotation scans
Absorption correction: none
5870 measured reflections
3010 independent reflections

1301 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int}$ = 0.0706
$\theta_{\max}$ = 24.20°
$h = -10 \rightarrow 9$
$k = -12 \rightarrow 11$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R(F)$ = 0.0574
$wR(F^2)$ = 0.1442
S = 0.970
3008 reflections
291 parameters
All H-atom parameters refined, except for methyl H atoms which were refined as riding

$w = 1/[\sigma^2(F_o^2) + (0.0285P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.149 e Å^{-3}
$\Delta\rho_{\min}$ = −0.180 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (III)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
N3	−0.2143 (3)	1.0398 (3)	0.3901 (3)	0.0562 (14)
N5	−0.1556 (3)	0.8526 (3)	0.0884 (3)	0.0556 (2)
N12	0.2040 (3)	0.8593 (3)	0.1209 (3)	0.0430 (12)
N13	0.1212 (3)	0.9557 (3)	0.1868 (3)	0.0434 (12)
C1	−0.0352 (4)	0.9529 (4)	0.2110 (4)	0.0438 (2)
C2	−0.1294 (4)	1.0014 (4)	0.3092 (4)	0.0436 (2)
C4	−0.0921 (4)	0.8967 (4)	0.1397 (4)	0.0442 (2)
C6	0.4039 (4)	0.8643 (4)	0.3083 (4)	0.0429 (14)
C7	0.5341 (4)	0.8669 (4)	0.3659 (4)	0.0555 (2)
C8	0.3054 (4)	0.7660 (4)	0.3931 (4)	0.0511 (2)
C11	0.3494 (4)	0.8394 (4)	0.1028 (4)	0.0414 (14)
C14	0.1799 (4)	1.0404 (4)	0.2174 (4)	0.0413 (14)
C15	0.3379 (4)	1.0045 (4)	0.2280 (4)	0.0428 (2)
C16	0.4338 (4)	0.8903 (4)	0.1649 (4)	0.0422 (2)
C21	0.4278 (4)	0.7639 (4)	0.0093 (4)	0.0411 (2)
C22	0.5756 (4)	0.6912 (4)	0.0109 (4)	0.0452 (14)
C23	0.6457 (4)	0.6182 (4)	−0.0772 (4)	0.0462 (14)
C24	0.5748 (4)	0.6194 (4)	−0.1728 (4)	0.0483 (14)
C25	0.4285 (4)	0.6966 (4)	−0.1775 (4)	0.0535 (2)
C26	0.3559 (4)	0.7668 (4)	−0.0869 (4)	0.0458 (14)
C27	0.6485 (4)	0.5394 (4)	−0.2677 (4)	0.0618 (2)
C31	0.0911 (4)	1.1678 (4)	0.2458 (4)	0.0415 (14)
C32	−0.0032 (4)	1.2627 (4)	0.1652 (4)	0.0442 (14)
C33	−0.0789 (4)	1.3841 (4)	0.1923 (4)	0.0509 (2)
C34	−0.0708 (4)	1.4132 (4)	0.3024 (4)	0.0537 (2)
C35	0.0237 (4)	1.3171 (4)	0.3821 (4)	0.0540 (2)
C36	0.1056 (4)	1.1976 (4)	0.3535 (4)	0.0440 (14)
C37	−0.1602 (4)	1.5418 (4)	0.3389 (4)	0.0824 (2)

Table 2. *Selected geometric parameters (Å, °) for (III)*

N3—C2	1.163 (5)	C1—C4	1.395 (6)
N5—C4	1.174 (5)	C6—C15	1.523 (6)
N12—N13	1.406 (4)	C6—C16	1.524 (6)
N12—C11	1.299 (5)	C11—C16	1.456 (6)
N13—C1	1.430 (5)	C14—C15	1.455 (6)
N13—C14	1.319 (5)	C15—C16	1.559 (6)
C1—C2	1.389 (6)		
N13—N12—C11	118.1 (3)	N12—C11—C21	115.1 (4)
N12—N13—C1	110.6 (3)	C16—C11—C21	120.3 (4)
N12—N13—C14	124.3 (3)	N13—C14—C15	119.1 (4)
C1—N13—C14	125.0 (3)	N13—C14—C31	122.6 (4)
N13—C1—C2	119.7 (4)	C15—C14—C31	118.2 (4)
N13—C1—C4	120.2 (4)	C6—C15—C14	120.9 (4)
C2—C1—C4	120.0 (4)	C6—C15—C16	59.3 (3)
N3—C2—C1	176.4 (4)	C14—C15—C16	115.3 (3)
N5—C4—C1	172.3 (4)	C6—C16—C11	121.4 (4)
C15—C6—C16	61.6 (3)	C6—C16—C15	59.2 (3)
N12—C11—C16	124.6 (4)	C11—C16—C15	113.8 (3)

Compound (V)

Crystal data

$C_{22}H_{17}N_3O$
M_r = 339.40

Mo $K\alpha$ radiation
λ = 0.71069 Å

Triclinic
$P\bar{1}$
$a = 8.9782\ (12)$ Å
$b = 9.3666\ (11)$ Å
$c = 12.043\ (2)$ Å
$\alpha = 76.538\ (10)^\circ$
$\beta = 76.584\ (11)^\circ$
$\gamma = 63.662\ (9)^\circ$
$V = 873.0\ (2)$ Å^3
$Z = 2$
$D_x = 1.291$ Mg m^{-3}
D_m not measured

Cell parameters from 1661 reflections
$\theta = 2.45\text{–}24.11^\circ$
$\mu = 0.08$ mm^{-1}
$T = 170\ (2)$ K
Distorted hexagonal prism
0.18 × 0.18 × 0.05 mm
Ruby red

Data collection

Stoe IPDS diffractometer
Rotation scans
Absorption correction: none
5113 measured reflections
2629 independent reflections

1743 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0321$
$\theta_{\rm max} = 24.11^\circ$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R(F) = 0.0329$
$wR(F^2) = 0.0714$
$S = 0.839$
2629 reflections
272 parameters
All H-atom parameters refined, except for methyl H atoms which were refined as riding

$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.139$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.127$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (V)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O42	0.6514 (2)	0.3315 (2)	0.43529 (10)	0.0423 (4)
N34	0.8775 (2)	0.27419 (2)	0.08240 (11)	0.0277 (5)
N45	1.1505 (2)	0.0943 (2)	−0.15804 (14)	0.0462 (6)
N47	1.2537 (2)	0.3133 (2)	0.0702 (2)	0.0536 (7)
C11	0.7179 (2)	0.2729 (2)	−0.06256 (14)	0.0297 (6)
C12	0.6267 (2)	0.1895 (2)	−0.0713 (2)	0.0371 (6)
C13	0.5932 (3)	0.1884 (2)	−0.1782 (2)	0.0447 (8)
C14	0.6499 (3)	0.2717 (2)	−0.2763 (2)	0.0460 (7)
C15	0.7396 (3)	0.3552 (2)	−0.2683 (2)	0.0435 (7)
C16	0.7737 (2)	0.3571 (2)	−0.1623 (2)	0.0364 (6)
C21	0.4508 (2)	0.2487 (2)	0.41124 (14)	0.0290 (6)
C22	0.3350 (2)	0.3224 (2)	0.5025 (2)	0.0350 (6)
C23	0.2014 (3)	0.2812 (2)	0.5499 (2)	0.0425 (7)
C24	0.1830 (3)	0.1654 (2)	0.5083 (2)	0.0437 (7)
C25	0.2991 (2)	0.0891 (2)	0.4200 (2)	0.0396 (7)
C26	0.4324 (2)	0.1307 (2)	0.3703 (2)	0.0328 (6)
C31	0.6777 (2)	0.2866 (2)	0.24646 (14)	0.0275 (6)
C32	0.6184 (2)	0.2830 (2)	0.15466 (2)	0.0294 (6)
C33	0.7420 (2)	0.2769 (2)	0.05316 (14)	0.0279 (6)
C35	0.8490 (2)	0.2875 (2)	0.20977 (14)	0.0286 (6)
C41	0.5958 (2)	0.2925 (2)	0.36818 (2)	0.0312 (6)
C43	1.0358 (2)	0.2453 (2)	0.01608 (14)	0.0303 (6)
C44	1.0936 (2)	0.1620 (2)	−0.0791 (2)	0.0322 (6)
C46	1.1523 (2)	0.2843 (2)	0.0480 (2)	0.0375 (6)
C48	0.8466 (2)	0.4470 (2)	0.2233 (2)	0.0399 (6)
C49	0.9812 (2)	0.1390 (2)	0.2690 (2)	0.0378 (6)

Table 4. *Selected geometric parameters (Å, °) for (V)*

O42—C41	1.234 (3)	C31—C32	1.347 (3)
N34—C33	1.331 (3)	C31—C35	1.502 (3)
N34—C35	1.521 (2)	C31—C41	1.481 (2)
N34—C43	1.401 (3)	C32—C33	1.441 (3)
N45—C44	1.155 (3)	C43—C44	1.405 (3)
N47—C46	1.158 (3)	C43—C46	1.402 (3)
C33—N34—C35	110.51 (2)	N34—C35—C48	109.89 (2)
C33—N34—C43	128.68 (14)	N34—C35—C49	108.76 (14)
C35—N34—C43	120.44 (2)	O42—C41—C21	119.49 (2)
C32—C31—C41	128.85 (2)	O42—C41—C31	119.43 (2)
C35—C31—C41	121.06 (2)	C21—C41—C31	121.07 (2)
C31—C32—C33	109.58 (2)	N34—C43—C44	122.34 (2)
N34—C33—C11	126.96 (2)	N34—C43—C46	121.48 (2)
N34—C33—C32	109.05 (2)	C44—C43—C46	115.89 (2)
C11—C33—C32	123.99 (2)	N45—C44—C43	175.7 (2)
N34—C35—C31	100.66 (2)	N47—C46—C43	176.9 (2)

Methyl H atoms were placed in idealized positions and torsion angles were refined based on difference electron-density synthesis, with a common isotropic displacement parameter. All other H atoms were placed in idealized positions and refined with a common isotropic displacement parameter for similar groups.

For both compounds, program(s) used to solve structures: *SIR*92 (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *PLATON* (Spek, 1990) and *PLUTON* (Spek, 1991); software used to prepare material for publication: *PLATON*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles for compounds (III) and (V) have been deposited with the IUCr (Reference: JZ1114). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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