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1,4-Shift of Methoxycarbonyl Group in *N*-[1,2,3,4,5-Pentakis(methoxycarbonyl)cyclopentadienyl]-*N*,*N'*-diaryl Benzamidines

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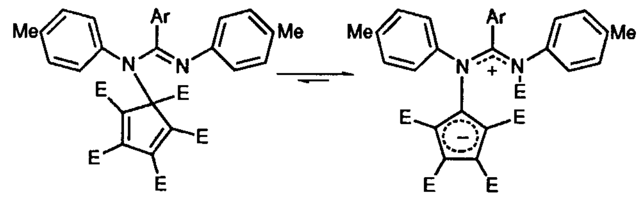
Novel cyclopentadiene *N*-ylides have been obtained by a thermal 1,4-shift of the methoxycarbonyl group in *N*-(1,2,3,4,5-pentakismethoxycarbonylcyclopentadienyl)-*N*,*N'*-diaryl benzamidines and their structure has been proved by ^{1}H NMR spectroscopy and X-ray analysis.

It has been found previously[1] that *N*-[1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadienyl]-*N*,*N'*-diarylamidines **1** undergo fast degenerate 1-N,3-N hetero-Cope rearrangements with free activation energies falling within the range 20.4–22.7 kcal mol^{-1}.† At elevated temperatures a slow accumulation of a coloured by-product has also been observed, whose nature remained unproven.

In the present study the origin of the reaction leading to the formation of this by-product has been identified as a novel thermal rearrangement involving an intramolecular 1,4-(C→N)-shift of the methoxycarbonyl group E linked to an sp^3-hybridized ring carbon.



1 **2**

E = CO_2Me
a; Ar = 4-$NO_2C_6H_4$
b; Ar = 4-BrC_6H_4
c; Ar = Ph
d; Ar = 4-MeC_6H_4
e; Ar = 4-$MeOC_6H_4$

Scheme 1

Upon heating *o*-dichlorobenzene solutions of benzamidines **1** at 120–140 °C for 0.5–1 h, equilibrium is established with the *N*-ylides **2**, as shown by the emergence of a set of signals attributable to isomer **2** (Table 1).

The reversible **1** ⇌ **2** rearrangement does not show a concentration dependence. Both the direct and reverse reaction are first order. Table 1 contains values of the rate constants and free activation energies as determined in *o*-dichlorobenzene solution at 120 °C. Whereas the rate of the **2**→**1** rearrangement is virtually unaffected by substitution at the C-aryl group of the amidine triad, that of the **1**→**2** reaction and the equilibrium content of **2** are decreased when electron-withdrawing substituents are introduced into the C-aryl moiety.

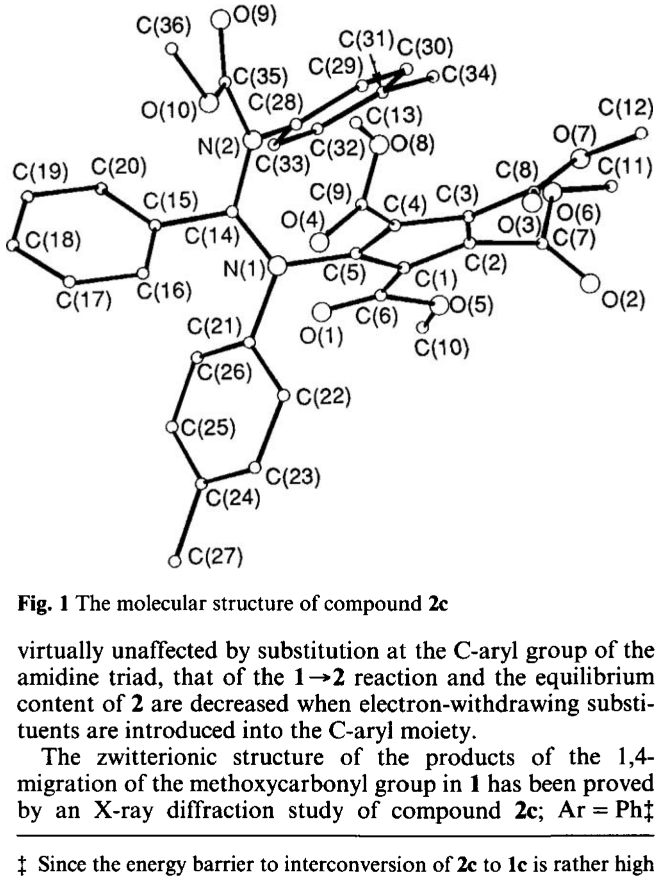


Fig. 1 The molecular structure of compound **2c**

The zwitterionic structure of the products of the 1,4-migration of the methoxycarbonyl group in **1** has been proved by an X-ray diffraction study of compound **2c**; Ar = Ph‡

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† 1 cal = 4.184 J.

‡ Since the energy barrier to interconversion of **2c** to **1c** is rather high (27.7 kcal mol^{-1}, Table 1) it is possible to achieve their separation by repeated crystallization (5 times) in a suitable solvent [acetone–hexane (1:3)]. Compound **2c**: red crystals, m.p. 160–162 °C; ^{1}H NMR [$^2H_4$]*o*-dichlorobenzene) δ 1.99(3H,s,CH_3), 2.09(3H,s,CH_3), 3.29(3H,s,OCH_3), 3.60(6H,s,OCH_3), 3.63(6H,s,OCH_3), 7.59–8.42(13H,m,aromatic H); IR (nujol) ν/cm^{-1} 1760, 1725, 1710 (C=O), 1670, 1620, 1590; UV (benzene) λ_{max}/nm 370 (ϵ 12 700), 475 (10 400). Compound **2c** gave satisfactory elemental analysis.

Table 1 Equilibrium and rate constants of **1** ⇌ **2** rearrangements of compounds **1a–e** in *o*-dichlorobenzene at 120 °C

					$\Delta G^{\ddagger}$/kcal mol^{-1}	
Compound[a]	M.p./°C	$K = [2]^c/[1]^d$	$10^3[k(1\rightarrow2)/s^{-1}]$	$10^3[k(2\rightarrow1)/s^{-1}]$	**1**→**2**	**2**→**1**
1a	150–152	0.25	0.8	3.2	28.8	27.6
1b	148–150	0.31	1.0	3.2	28.6	27.6
1c	142–143	0.40	1.2	3.0	28.4	27.7
1d	110–112	0.53	1.6	3.0	28.1	27.7
1e[b]	176–177	0.66	2.1	3.2	28.0	27.6

[a] Compounds **1a–e** gave satisfactory elemental analyses. [b] $\Delta H^{\ddagger}$ (**1**→**2**) 21.3 kcal mol^{-1}, $\Delta S^{\ddagger}$ (**1**→**2**) − 16.9 cal mol^{-1} K^{-1}. [c] With the exception of **2c** the *N*-ylides were not preparatively isolated. ^{1}H NMR (*o*-dichlorobenzene, 30 °C): **2a** δ 1.90(3H,s,CH_3), 2.01(3H,s,CH_3), 3.47(3H,s,OCH_3), 3.72(6H,s,OCH_3), 3.78(6H,s,OCH_3); **2b** δ 1.84(3H,s,CH_3), 1.99(3H,s,CH_3), 3.25(3H,s,OCH_3), 3.53(6H,s,OCH_3), 3.54(6H,s,OCH_3); **2c** see footnote ‡; **2d** δ 1.72(3H,s,CH_3), 1.90(3H,s,CH_3), 2.00(3H,s,CH_3), 3.25(3H,s,OCH_3), 3.54(6H,s,OCH_3), 3.55(6H,s,OCH_3); **2e** δ 1.98(3H,s,CH_3), 1.99(3H,s,CH_3), 3.03(3H,s,OCH_3), 3.26(3H,s,OCH_3), 3.52(6H,s,OCH_3), 3.53(6H,s,OCH_3). [d] ^{1}H NMR (*o*-dichlorobenzene, 30 °C): **1a** δ 1.86(3H,s,CH_3), 2.13(3H,s,CH_3), 3.57(3H,s,OCH_3), 3.78(6H,s,OCH_3), 3.82(6H,s,OCH_3); **1b** δ 1.86(3H,s,CH_3), 2.11(3H,s,CH_3), 3.31(3H,s,OCH_3), 3.40(6H,s,OCH_3), 3.65(6H,s,OCH_3); **1c** δ 1.93(3H,s,CH_3), 2.18(3H,s,CH_3), 3.33(3H,s,OCH_3), 3.45(6H,s,OCH_3), 3.69(6H,s,OCH_3); **1d** δ 1.88(3H,s,CH_3), 1.94(3H,s,CH_3), 2.14(3H,s,CH_3), 3.29(3H,s,OCH_3), 3.40(6H,s,OCH_3), 3.66(6H,s,OCH_3); **1e** δ 1.89(3H,s,CH_3), 2.13(3H,s,CH_3), 3.31(3H,s,OCH_3), 3.34(3H,s,OCH_3), 3.38(6H,s,OCH_3), 3.65(6H,s,OCH_3).

(Fig. 1).§ A marked similarity of the C–C bond lengths in the cyclopentadiene ring 1.374(9)–1.437(8) Å was observed, which is characteristic of similarly substituted cyclopentadiene anions.[2] Also the lengths of the C–N bonds in the amidine fragment are very close in value, 1.327(5) and 1.369(7) Å, typical of those found in other amidine cations.[3,4]

The steric crowdedness of the molecule of **2c** manifests itself in the rotation of the cyclopentadienyl ring at 72.2(2)° to the amidine plane and also in the acoplanar conformations of the methoxycarbonyl groups. Some of the intramolecular contacts are considerably shortened, *e.g.* C(1)···C(28), C(4)···C(30), C(5)···C(28) and C(5)···C(33) measure 3.268(8), 3.315(5), 2.880(7) and 3.247(8) Å respectively. By contrast, no short-distance intermolecular contacts were found in the unit cell of **2c** (Fig. 2).

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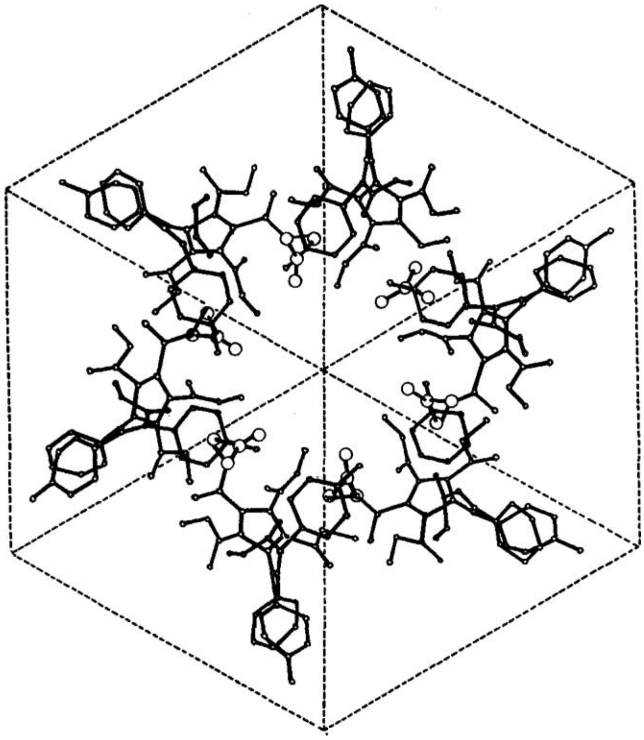

Fig. 2 The unit cell of compound **2c**. No short intermolecular contacts were found in the unit cell. Apart from localized acetone molecules occupying the common position, a cavity with a diameter of 12–16 Å exists along the C_3-axis, in which disordered solvent molecules are probably located

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§ *Crystal data* for **2c**: $C_{36}H_{34}N_2O_{10}\cdot C_3H_6O\cdot X$, rhombohedral, space group $R\bar{3}$, $a = b = c = 18.583(5)$ Å, $\alpha = \beta = \gamma = 100.96(3)°$, $V = 6012.6(8)$ Å^3, $Z = 6$, crystal size 0.4 × 0.3 × 0.3 mm. 7175 Independent reflections were measured with $I > 1\sigma$ using KM-4 diffractometer (λ Cu-Kα = 1.5424Å, ω scan technique, $\theta < 70°$). Programs used were from the SHELX 86[5] and SHELX 76[6] packages, the latter being employed for a block-diagonal least-squares refinement procedure based on 4144 reflections with $F^2 > 6\sigma$. Hydrogen atoms in $C_{36}H_{34}$ N_2O_{10} and C_3H_6O were geometrically defined and used in refinement procedure with fixed thermal parameters. Since the second molecule of the solvent is strongly disordered, a model molecule was used containing 'carbon atoms' whose positions were taken from the difference map and only population multiplicities of these were refined. Unlocating atoms of the solvent because of their strong disorder in the large cavity (see Fig. 2) led to a low accuracy in the structure refinement and to high values of the R-factors ($R = 0.095$, $R_W = 0.104$, $R_{INT} = 0.137$, $\Delta\rho_{max} = 0.74$ e Å^{-3}). Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *J. Chem. Soc., Chem. Commun.*, Issue No. 1, 1991.

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