Structure Determination of the Adducts of 1,3-Di-*tert*-butyl- and 1,2,3,4-Tetraphenyldiazocyclopentadiene with Dimethyl Acetylenedicarboxylate by Carbon-13 NMR

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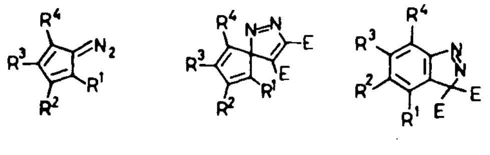
Received December 10, 1987

It is shown by NMR spectroscopic arguments, including two-dimensional ^{13}C INADEQUATE experiments, that the adducts of the diazocyclopentadienes 1a and 1b with dimethyl acetylenedicarboxylate have the 3*H*-indazole structure 3 and not, as was reported in the case of 1b, the spirononatetraene structure 2.

It is well-known from several investigations — the first has been published by J. van Alphen in 1943 1) — that the reaction of diazacyclopentadienes with dimethyl acetylenedicarboxylate (DMAD) leads to different products depending on substituents and reaction conditions 2–5).

In the course of investigations on 1,3-di-*tert*-butyldiazocyclopentadiene 6) (**1a**), we performed this reaction following the procedure described in detail in ref. 3) for the tetraphenyl compound **1b**; in this case structure **2b** has been attributed to the product 3a). But since there arose some doubts concerning this spirononatetraene structure **2**, we undertook an NMR investigation of the reaction products of **1a** and **1b** with DMAD.

Scheme 1



1 2 3

1–3	R¹	R²	R³	R⁴
a	H	tBu	H	tBu
b	Ph	Ph	Ph	Ph

E = CO_2Me

The 300-MHz ^{1}H-NMR spectrum of the DMAD adduct of **1a** shows two singlets at δ_H = 1.38 and 1.65 (*tert*-butyl groups), only one OCH_3 absorption at δ_H = 3.38, and two doublets at δ_H = 7.54 and 7.68; these doublets appear somewhat outside the range expected for the olefinic protons of **2a**. Furthermore, in the region typical for sp^2-hybridized C atoms only seven signals are detected instead of eight, as is necessary for **2a**.

Similar observations not being in accordance with the proposed spirononatetraene structure **2** can be made in the NMR spectra of the DMAD adduct of **1b**, which has been prepared according to ref. 3) (m.p. 190°C; ref. 3) 191°C): again only one OCH_3 signal (^{1}H, ^{13}C) can be detected, more ^{13}C signals than would be required for the higher symmetric **2b** occur in the C(sp^2) region, and finally, only one C=O signal is observed. The latter fact holds, too, for the DMAD adduct of **1a**; this is established for both adducts from undecoupled ^{13}C-NMR spectra (δ_C values 163.6 and 162.5, respectively). Another feature common to the ^{13}C spectra of both adducts is a signal near δ_C = 100 (100.0 and 103.5, respectively).

Thus it can be concluded that both adducts, as well that from **1a** as that from **1b**, have the same structure. Moreover, putting together all NMR spectroscopic information, the 3*H*-indazole structure **3** may be deduced tentatively for the two compounds.

Further evidence in favour of this structure has been gained from ^{13}C spectra obtained under low-energy decoupling of the *tert*-butyl protons, so that the geminal and vicinal ^{13}C,^{1}H couplings of the sp^2-type carbons became observable. They are in accordance not with a five-membered ring, but with a benzene derivative 7).

As a final proof of the 3*H*-indazole structure, two-dimensional ^{13}C INADEQUATE experiments were performed on **3a** and **3b** 8). The contour plot of the 2D spectrum of **3a** shows all the connectivities of the benzene ring, its connection to C-3 as well as the bonding of this C atom to the equivalent carbonyl carbon atoms (Figure 1). Moreover, the isomer with the *tert*-butyl groups on C-4 and C-6 has to be excluded since C-3a is connected to a hydrogen-bearing carbon atom as in **3a**.

Table 1. ^{13}C-NMR data of **3a** and **3b**

		3a		**3b**	
Assignment	δ_C	Multipl.	*J*(C,H)	Assignment	δ_C
C-3	100.00	d	^3J(C-3,H-4) = 1.1 Hz	C-3	103.48
C-3a	135.27	s		C-3a	133.60
C-4	118.95	d,d	^1J(C-4,H-4) = 163.8 Hz ^3J(C-4,H-6) = 7.8 Hz	C-4	137.78
C-5	154.78	dec	^3J(C-5,CH_3) = 3.8 Hz	C-5	145.11
C-6	124.71	d,d	^1J(C-6,H-6) = 155.6 Hz ^3J(C-6,H-4) = 6.4 Hz	C-6	144.00
C-7	145.08	dec,d	^3J(C-7,CH_3) = 3.9 Hz ^2J(C-7,H-6) = 1.2 Hz	C-7	135.39
C-7a	154.82	d,d	^3J(C-7a,H-6) = 8.8 Hz ^3J(C-7a,H-4) = 6.1 Hz	C-7a	156.93
C=O	163.60	q	^3J(*C*O,OC*H*$_3$) = 4.0 Hz	C=O	162.51
OCH_3	53.79	q	^1J(O*CH*$_3$) = 148.5 Hz	OCH_3	53.41
7-*C*$(CH_3)_3$	36.03	dec,d	^2J(C,CH_3) = 3.8 Hz ^3J(C,H-6) = 3.5 Hz	Phenyl *i*-C	138.58 138.45 137.78 135.51
5-*C*$(CH_3)_3$	35.58	dec,t	^2J(C,CH_3) = 3.8 Hz ^3J(C,H-4) = 3.3 Hz ^3J(C,H-6) = 3.3 Hz	Phenyl *o*-C	131.26 131.19 130.82 129.72
				Phenyl *m*-C	127.45 127.18 127.07 126.79
$(CH_3)_3$	31.62 31.44	q,dec	^1J(CH_3) = 126.1 Hz ^3J(CH_3,C*H*$_3$) = 3.7 Hz	Phenyl *p*-C	127.37 127.10 126.21 126.05

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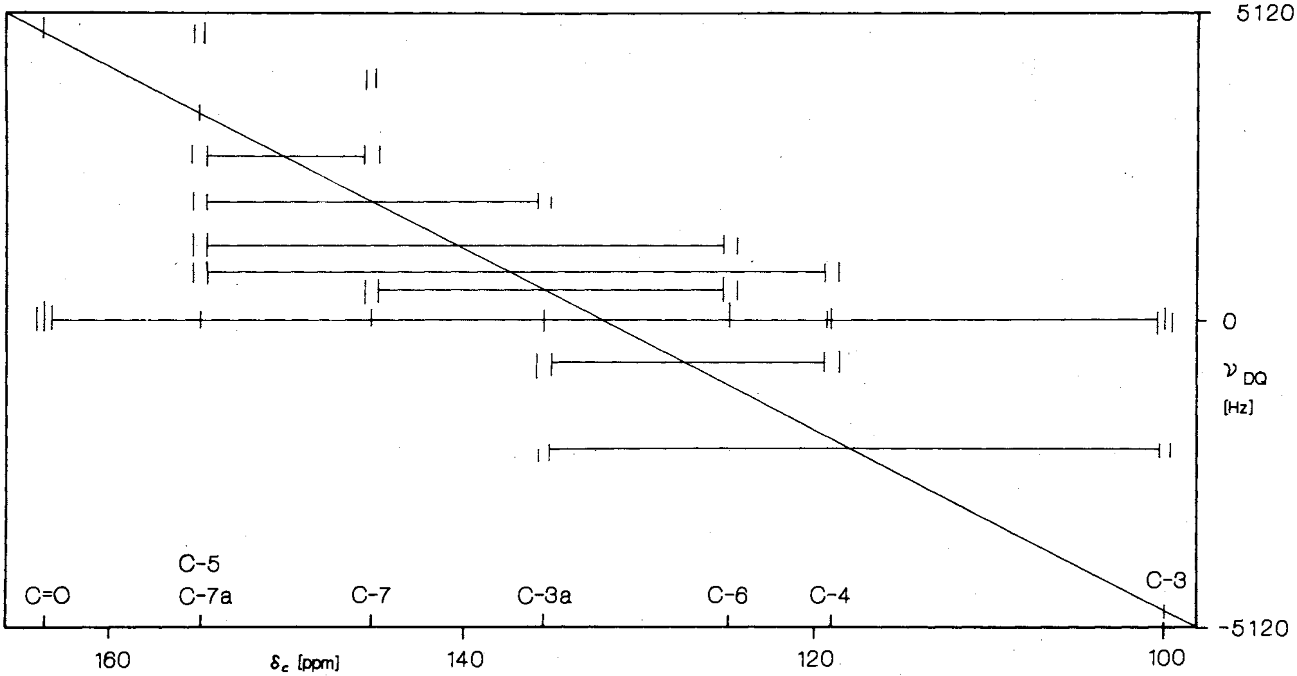
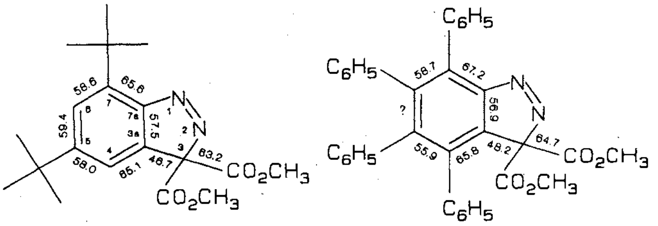


Figure 1. 2D ^{13}C NMR INADEQUATE spectrum of **3a** (75 MHz, solvent $CDCl_3$, contour plot)

In the case of **3b** all connectivities within the 3*H*-indazole system except for the one between C-5 and C-6 (strongly coupled AB system, $J/\Delta = 0.7$) could be detected[*]. Thus, the 3*H*-indazole structure **3** is unequivocally established not only for **3a**, but also for the tetraphenyl compound **3b**, contrary to ref.[3].

The 1D ^{13}C-NMR data of **3a** [δ_C and J(C,H)] and of **3b** (δ_C only) are presented in Table 1, and the ^1J(C,C) values, as determined from the ^{13}C,^{13}C satellites of the 2D data matrices, can be read from the following scheme:

Scheme 2

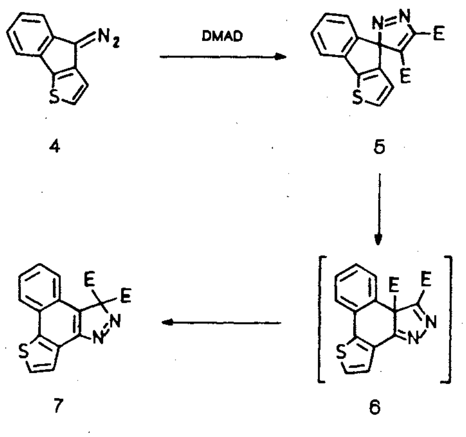


The ^{13}C-NMR spectrum of the DMAD adduct of **1b** has been reported, the δ_C values being in agreement with those measured by us; however, they are not complete and have been assigned on the basis of the spirononatetraene structure **2b**[9].

As a consequence of our structure revision the discussion about a possible spiro conjugation in **2b**[3a] as well as that about the mechanism of the photoreaction yielding benzocyclopropenes[10-12] has no further basis, at least for the tetraphenyl-substituted compound: the 3*H*-indazole **3b** is not, as has been postulated in these papers, an intermediate of the photoreaction, but represents just the educt (cf. also ref.[3b]).

Concerning the mechanism of the formation of **3**, an example described in the literature[5] may be presented, where the spiro compound **5** could be isolated as a thermally unstable substance. Its conversion into **7** is interpreted as taking place via a Van Alphen-Hüttel rearrangement[13] to **6** followed by migration of a carbomethoxy group[5].

Scheme 3



We thank Priv. Doz. Dr. *R. Benn*, Mülheim, for an additional 2D ^{13}C INADEQUATE experiment on **3a** at a ^{13}C frequency of 100 MHz and the *Wella AG*, Darmstadt, for financial support.

Experimental

^{1}H- and ^{13}C-NMR spectra were obtained on a Bruker WM 300 NMR spectrometer at 300.133 and 75.469 MHz respectively. For the 2D-INADEQUATE experiments a 10-mm tube was filled with a solution of ca. 700 mg of **3a** (**3b**: ca. 1 g) and 10 mg of $Cr(acac)_3$ in 2.5 ml of $CDCl_3$, and the pulse sequence of Mareci and Freeman[8] was employed, using a refocusing delay τ of 4.55 ms, which corre-

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[*] *Note added in proof (10.2.1988):* The coupling between C-5 and C-6 in **3b** could be detected at 500 MHz [J(C-5,C-6) = 60.0 Hz], all other J(C,C) values being the same within experimental error (experiment by courtesy of P. Dvortsak, Bruker GmbH).

sponds to a J(C,C) value of 55 Hz. The spectral width in the f_2 dimension was 5100 Hz, and 64 different experiments of size 8 K and with 160 FIDs each (**3a**: 320) were performed. The relaxation delay was 20 s (**3a**: 9 s) so that the total measuring time amounted to about 60 hours (over weekend). 2D Fourier transformation was performed after zero filling in f_1 and applying a shifted sine bell function in both dimensions.

CAS Registry Numbers

1a: 112794-61-3 / **1b**: 4828-84-6 / **2b**: 23227-65-8 / **3a**: 112794-59-9 / **3b**: 112794-60-2 / DMAD: 762-42-5

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[346/87]

Dieses Heft wurde am 5. Mai 1988 ausgegeben.

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Verantwortlich für den Inhalt: Prof. Dr. Hans Musso, Karlsruhe. Redaktion: Dr. Robert Temme, Weinheim.

VCH Verlagsgesellschaft mbH (Geschäftsführer: Prof. Dr. Helmut Grünewald und Hans Dirk Köhler), Pappelallee 3, Postfach 1260/1280, D-6940 Weinheim.

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