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NMR-STUDY OF CYCLOBUTENE DERIVATIVES

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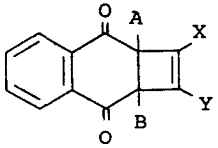
The NMR spectrum of unsubstituted cyclobutene has been analysed by HILL and ROBERTS 1). NMR data for cyclobutenes and other C_4-ring compounds have been reviewed 2). The compounds I - XVIII, which have been obtained by photoaddition of 1.4-naphthoquinones to acetylenes 3) provide a sufficient number of examples for a systematic NMR study of cyclobutene derivatives. The relevant τ-values are compiled in table 1. The assignments are based on chemical shifts and coupling constants. Further confirmations have been obtained by way of comparison; for example, the signals of both A and B protons in III (X = Y = Me) and VI (X = Y = Ph) are located at 6.19 and 5.52 τ, respectively. The corresponding signals in V are observed at 6.07 and 5.63 τ. Accordingly the higher field signal is to be assigned to the proton adjacent to the methyl (Y), the lower field signal to that adjacent to the phenyl (X) group.

For the H and Me on the cyclobutene ring we determined increments of chemical shifts ($\Delta\tau$) due to the replacement of a neighbouring hydrogen atom by a methyl or phenyl group and of a methyl by a phenyl group (table 2). For example, comparison of IV and IX shows that the signals of the proton at position B is shifted 0.28 ppm to higher field when the H at position A is replaced by Me. The number of examples from which the $\Delta\tau$ values are averaged ranges from three to seven.

Table 1:

Chemical shifts[4) (τ) of hydrogen atoms and methyl groups on the cyclobutene ring in I - XVIII*]



I - XVIII

A,B = H,Me X,Y = H,Me,Ph

	I	II	III	IV	V	VI
A	H 5.86	H 6.06-6.03	H 6.19	H 5.48	H 5.63	H 5.52
B	H	H	H	H 5.88	H 6.07	H
X	H 3.60	Me 8.23	Me 8.32	Ph -	Ph -	Ph -
Y	H	H 3.93	Me	H 3.43	Me 7.94	Ph -

	VII	VIII	IX	X	XI	XII
A	Me 8.42	Me 8.47	Me 8.17	Me 8.31	Me 8.22	Me 8.39
B	H 6.38	H 6.52	H 6.21	H 5.83	H 6.38	H 5.94
X	Me 8.32	Me 8.37-8.42	Ph -	H 3.42	Ph -	Me 8.04
Y	H 3.98	Me	H 3.43	Ph -	Me 7.98	Ph -

	XIII	XIV	XV	XVI	XVII	XVIII
A	Me 8.22	Me 8.50	Me 8.52	Me 8.22	Me 8.27	Me 8.20
B	H 5.82	Me 8.48	Me	Me 8.36	Me 8.42	Me
X	Ph -	Me 8.39	Me 8.49	Ph -	Ph -	Ph -
Y	Ph -	H 4.01	Me	H 3.47	Me 8.11	Ph -

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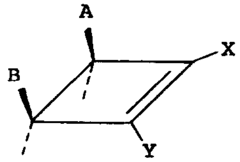
*) m.p.(°C): I (154-5), II (74-5), III (120-1), IV (137-8), V (136-7), VI (178-80), VII (117-8), VIII (96-7), IX (119-20), XI (102-3), XIII (116-7), XIV (108-9), XV (139-40), XVI (140-1), XVII (134-5), XVIII (165-6). X and XII have not yet been obtained in pure form.

Table 2: Average Δτ increments of H and CH_3 due to methyl and phenyl substitution of a neighbouring position.



Δτ of H at position B	
A: H → Me	$+0.33\pm0.03^{a}$
Y: H → Me	$+0.18\pm0.02^{b}$
Y: H → Ph	-0.40 ± 0.04^{b}
Y: Me → Ph	$-0.57\pm0.02^{b,e}$

Δτ of CH_3 at position A	
B: H → Me	$+0.05\pm0.02^{c,f}$
X: H → Me	$+0.06\pm0.02^{d}$
X: H → Ph	-0.15 ± 0.06^{d}
X: Me → Ph	-0.23 ± 0.06^{c}

Δτ of CH_3 at position X	
A: H → Me	$+0.11\pm0.02^{b}$
Y: H → Me	$+0.10\pm0.01^{d}$
Y: H → Ph	-0.28 ± 0.01^{d}
Y: Me → Ph	-0.38 ± 0.01^{d}

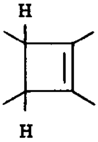
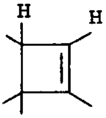
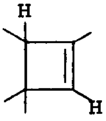
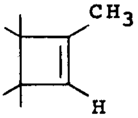
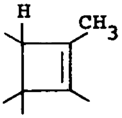
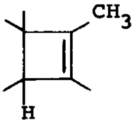
Number of examples: a) 7, b) 5, c) 6, d) 3.
e) For H at position X, Δτ = -0.53±0.03 due to the change Y: Me → Ph
f) exception: XIII - XVIII Δτ = -0.02.

The small J/δ ratios allow the coupling constants to be calculated by first order analysis.

There is no detectable coupling between protons of methyl groups at position A and protons at position X, i.e. across four single bonds with one sp^2-hybridized C-atom [5)] in the H-C-C-$\underset{\|}{C}$-H grouping. For example, in XIV the signals of both methyl groups at position A and B are as sharp as the signals of the methyl group on the double bond at position X (half width 0.5 c/s). The same is true with XVI. On the other hand, comparatively strong coupling across four single bonds occurs between methyl protons at position X (Y) and protons at position A (B), cf. **5** in table 3.

In this case a sp^2-hybridized C-atom is located symmetrically (H-C-$\underset{\|}{C}$-C-H) in such a way that overlap between its p-lobe and the two C-H-bonds is possible.

Table 3: Coupling constants |J| of H and Me on the cyclobutene ring 4)

1 a)	**2** b)	**3** c)	**4**	**5**	**6**
					
3.9 (IV)	1.4 (VII)	0.7 (IV)	1.6 (VII)	~1.3 (VIII)	~2.2 (VIII)
4.0 (V)	1.75 (IX)	0.85 (X)	1.65 (XIV)	1.5 (V)	2.3 (XII)
	1.8 (IV)			1.6 (XI)	2.4 (V)
					2.5 (VII)

Coupling constants obtained for the unsubstituted cyclobutene are 1):

a) +4.65 b) +1.0 c) -0.35 c/s.

References

1) E.A. Hill and J.D. Roberts, J. Amer. Chem. Soc., **89**, 2047 (1967)

2) I. Fleming and D.H. Williams, Tetrahedron **23**, 2747 (1967)

3) S. Farid, W. Kothe and G. Pfundt, Tetrahedron Letters, preceding paper

4) All measurements were carried out at 60 Mc/s in $CDCl_3$ at ca. 40°C

5) Such couplings observed in some aldehydes appear to be very sensitive to changes in stereochemistry; cf. Sternhell's review on long range couplings 6)

6) S. Sternhell, Rev. Pure and Appl. Chem., **14**, 15 (1964)