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CONJUGATIVE AND HOMOCONJUGATIVE EFFECTS IN 2-HETEROBICYCLO[3.2.1]OCTA-3,6-DIENES

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Abstract—The ^{1}H-NMR, ^{13}C-NMR and photoelectron spectra of a variety of 2-heterobicyclo[3.2.1]octa-3,6-dienes **6** give evidence of conjugative and homoconjugative effects in these compounds, but there is no suggestion from the data of any *special* contribution from the $(4n+2)\pi$ neutral bishomoaromatic system. Reaction of the dienes **6** with TCNE invariably yielded the product of [2+2] addition in cases where a fully characterisable product was obtained.

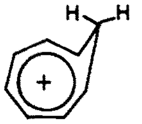
It is well known that special homoconjugative effects operate in cationic and anionic species containing a total of $(4n+2)\pi$-electrons in interrupted cyclic conjugation where the geometry allows orbital interaction to occur through space.[1] Such effects have been termed "homoaromatic" and theoretical treatments of homoaromaticity have been made.[2,3] Species such as the homotropylium cation 1[4] and the bicyclo[3.2.1] octadienyl anion 2[5] are archetypal homoaromatic compounds and are termed monohomoaromatic and bishomoaromatic respectively. Homoaromatic effects of comparable magnitude to those found with charged species have not been observed in neutral molecules and this has been explained in terms of the closeness in energy of the orbitals interacting through space in the charged species compared to those same orbitals in the neutral molecules.[6]

It has been a point of considerable interest over recent years to systhesise neutral molecules with $(4n+2)\pi$-electrons in interrupted conjugation which might show homoaromatic effects. The classical example of such a compound, *cis,cis cis* - cyclonona - 1,4,7 - triene 3, showed no evidence of neutral trishomoaromatic character from X-ray analysis,[7] NMR studies,[8] or heats of hydrogenation,[7a] although it has been claimed that significant homoconjugative interaction is shown by photoelectron spectroscopy.[9] Triquinacene 4 appears to show a smaller homoconjugative interaction than the triene 3[10] and this has been explained as being due to geometrical considerations.[11] The neutral homoaromatic compound elassovalene 5 has been shown to exhibit effects which might be ascribed to homoaromaticity in the bridged portion of the molecule using ^{1}H NMR and photoelectron spectra, and diamagnetic susceptibility measurements.[12]

It has been claimed that the aromaticity of the 6π-excessive heterocyclic compounds, furan, pyrrole and thiophene can be extended to analogues with 10,[13] 14,[14] and more[15] π-electrons and so there is a parallel between the heterocyclic compounds and their carbocyclic counterparts, the annulenes. Further, the anion 2 has properties which can be explained if it is considered to be the bishomoaromatic analogue of the cyclopentadienyl anion.[5] It therefore seemed of interest to prepare the bishomoaromatic analogues (**6**, X = O, NR and S) of furan, substituted pyrroles, and thiophene to see if they might have any properties suggestive of bishomoaromatic character. We have synthesised a variety of these compounds[16] and now report the results of investigation of their ^{1}H NMR, ^{13}C NMR and photoelectron (PE) spectra. During the course of our work some of the compounds of the azaseries (**6**, X = NR) were prepared[17] and it was claimed that there was some evidence of non-bonded interactions between the two formally isolated chromophores in these compounds.

^{1}H and ^{13}C NMR spectra. Assignments of chemical shifts in the ^{1}H NMR spectra of the various compounds are summarised in Table 1. In all of the compounds examined, the olefinic protons H_6 and H_7 were doublets of doublets, $J_{1,7}$ 2–3 Hz, $J_{5,6}$ 2.5–3 Hz and $J_{6,7} \sim 6$ Hz. Invariably irradiation at the lowest field non-olefinic proton H_1 removed the coupling H_1–H_7 and irradiation at the frequency assigned to proton H_5 removed the coupling H_5–H_6. Irradiation at either H_6 or H_7 removed the H_6–H_7 coupling from the other proton signal. The proton H_3 was usually the lowest field olefinic proton and was a doublet $J_{3,4} \sim 7$ Hz with occasionally long range coupling with H_1 in evidence. Double irradiation verified these assignments. Proton H_4 was a basic triplet on which additional long range coupling was superimposed. Decoupling was achieved by irradiation at either H_3 or H_5. The bridge protons H_8 invariably appeared as a clean AB doublet and a multiplet. Since long range coupling has been reported[18] between H_4 and H_{8a} in the diene **10**, we irradiated at H_4 in the Δ^3-ene (7, X = O) causing the H_8 multiplet to simplify to a doublet of triplets. Irradiation at H_1 and H_5 in the series also caused the H_8 multiplet to be decoupled. Geometrical arguments[19] for the diene (**6**, X = NSO$_2$Ph) suggest that since the proton H_{8a} has a dihedral angle of 55°–60° with H_1 and H_5, it should show maximum coupling while since the proton H_{8s} has a dihedral angle of 90° with H_1 and H_5, the only coupling to be expected would be geminal coupling. We therefore assigned H_{8s} to the doublet and H_{8a} to the multiplet in the series and this is in keeping with assignments in the diene (**6**, X = CH$_2$).[5b,5c] Since the shifts of the protons within the ring current of elassovalene 5 had been useful in assigning neutral bishomoaromatic effects, assignment of H_{8a} and H_{8s} with confidence was important to our study.

On comparing shift values between the 3-ene (7, X = O) and the diene (**6**, X = O) in the oxa-series, very little effect was noted on the H_3 $(\tau+0.24)$, H_4 $(\tau-0.12)$ and H_{8a} $(\tau+0.04)$ resonances on introduction of the Δ^6-π-



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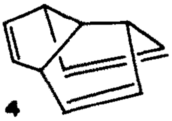

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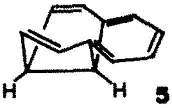

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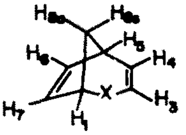

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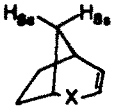

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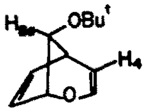

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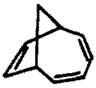


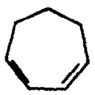
12

Table 1. Proton NMR spectra of 2-heterobicyclo[3.2.1]octanes, enes and dienes†

COMPOUND	H_1	H_3	H_4	H_5	H_6	H_7	H_{8a}	H_{8s}	SOLVENT
DIENE (6, X = O)	5.15	4.23	5.06	7.5	3.61	4.62	8.30		CCl_4
	5.13	4.20	5.0	7.4	3.56	4.62			$CDCl_3$
Δ^3-ENE (6, X = O)	5.44	3.96	5.12	7.7			8.83	8.36	$CDCl_3$
DIENE (6, X = NSO_2Ph)	5.27	3.74	4.76	7.36	3.94	4.82	8.28	8.68	$CDCl_3$
Δ^3-ENE (7, X = NSO_2Ph)	5.56	3.57	4.77	7.71			8.68	8.87	$CDCl_3$
Δ^6-ENE (8, X = NSO_2Ph)	5.36			7.39	4.0	4.85	8.10	8.39	$CDCl_3$
SAT^D (9, X = NSO_2Ph)	5.70			7.75					CCl_4
DIENE (6, X = NCO_2Me)	4.97	3.64	4.86	7.28	3.85	4.54	8.28		$CDCl_3$
Δ^3-ENE (7, X = NCO_2Me)	5.28	3.48	4.88	7.60			8.38	8.20	$CDCl_3$ (+60°)
Δ^6-ENE (8, X = NCO_2Me)	5.08			7.30	3.79	4.12	8.09	8.47	$CDCl_3$
SAT^D (9, X = NCO_2Me)	5.43			7.8					$CDCl_3$
DIENE (6, X = NMe)	6.22	4.46	5.20		3.88	4.80			$CDCl_3$
DIENE (6, X = NEt)	6.22	4.58	5.51	7.58	4.15	5.02	8.36	8.48	CCl_4
DIENE (6, X = NBu^t)	5.83	4.22	5.52	7.48	4.18	5.07	8.34	8.46	
Δ^3-ENE (7, X = NMe)	6.44	4.47	5.47	6.71					$CDCl_3$ (−40°)
Δ^6-ENE (8, X = NH)	6.35			7.40	3.89	4.22	8.12	8.44	$CDCl_3$
Δ^6-ENE (8, X = NMe)	6.54			7.47	3.84	4.14	8.27	8.40	$CDCl_3$ (−40°)
SAT^D (9, X = NBu^t)	6.57			7.83					$CDCl_3$
DIENE (6, X = S)	6.58	4.31	4.32	7.24	4.38	4.52	7.80	8.12	CCl_4
	6.45	4.15	4.18	7.16	4.23	4.37	7.84	8.06	$CDCl_3$
Δ^3-ENE (7, X = S)	6.79	4.16	4.16	7.57					$CDCl_3$
SAT^D (9, X = S)	7.0			7.0					CCl_4
DIENE (6, X = SO_2)	5.95	3.30	3.30	6.93	3.86	4.30	7.40	7.06	$CDCl_3$

† Chemical shift values in τ from an internal TMS standard

13



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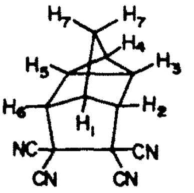

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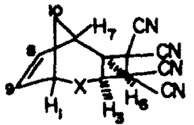

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bond. Similarly shifts were small for the olefinic protons and the bridge proton immediately over the double bond in the sulphonamide (6, X = NSO_2Ph) (H_3 τ + 0.17, H_4 −0.01, H_6 −0.06, H_7 −0.03, H_{8a} −0.19, H_{8s} + 0.18) compared to its dihydro-derivatives. The urethane series again showed small shifts (H_3 τ + 0.16, H_4 − 0.02, H_6 + 0.06, H_{8s} + 0.19, H_{8a} − 0.19) for all but the olefinic proton H_7 which showed an appreciable shielding of + 0.42 ppm.

If homoconjugative effects were to be appreciable then we might expect to see larger spectral shifts in the N-alkyl- and thia-dienes (6, X = NR and S). In the N-methyl series shifts were again small (H_3 τ − 0.01, H_4 − 0.27, H_6 + 0.04) for all but the olefinic proton H_7 which again showed appreciable shielding (+ 0.66 ppm). Although comparison of the bridge protons in this unstable series was not easy, it is evident from Table 1 that shifts were not large. The thia-series was unfortunately incomplete but shifts on H_3 and H_4 were very small on converting the 3-ene (7, X = S) to the diene (6, X = S). Very large shifts were apparent in the protons, H_6, H_7 and H_{8a}, which were transannular to the heteroatom on oxidation of the diene (6, X = S) to the sulphone (6, X = SO_2) but the change in electronegativity here makes differentiation of through-bond from through-space effects difficult.

Arguments for ring current effects based on ^{13}C NMR spectral shifts have been convincing for some compounds[20,21] although it is generally felt that ring current effects on ^{13}C shifts are small and are superimposed on other stronger effects.[22,23] Our assignments for the ^{13}C NMR spectral shifts of the 2 - heterobicyclo[3.2.1]octa - 3,6 - dienes 6 and their derivatives are summarised in Table 2. The time scale required to collect ^{13}C NMR spectra did not allow the spectra of all of the unstable compounds in the N-alkyl series to be obtained and ^1H NMR spectra were checked before and after all ^{13}C NMR spectral runs. The spectra of the dienes (6, X = O) and (6, X = N-alkyl) were complicated by the presence of the Cope-rearranged product 11. Spectra were proton decoupled and off-resonance decoupled and our assignments had the expected proton coupling. In the diene (6, X = O), C_3, C_4, C_5 and C_6 were assigned with certainty using specific proton decoupling and this technique was used to assign C_3, C_4, C_5, C_6 and C_7 in the diene (6, X = NSO_2Ph); C_6 and C_7 in the 6-ene (8, X = NSO_2Ph); C_3, C_4 and C_8 in the 3-ene (7, X = NSO_2Ph); and C_1, C_3, C_4 and C_5 in the 3-ene (7, X = NCO_2Me).

Table 2. ^{13}C NMR spectra of 2-heterobicyclo[3.2.1]octanes, enes and dienes

COMPOUND	CHEMICAL SHIFTS IN PPM FROM INTERNAL TMS							SOLVENT
	C_1	C_3	C_4	C_5	C_6	C_7	C_8	
DIENE (6, X = O)	79.7	140.5	105.8	36.2	142	119.8	69.6	$CDCl_3$
Δ^3-ENE (7, X = O)	77.7	140.8	107.8	36.2			31.9	$CDCl_3$
DIENE (6, X = NSO_2Ph)	59.7	139.2	110.8	35.8	121.2	121.7	34.6	$CDCl_3$
Δ^3-ENE (7, X = NSO_2Ph)	56.4	123.0	116.0	33.2			35.5	$CDCl_3$
Δ^6-ENE (8, X = NSO_2Ph)	59.1			37.6	137.7	125.4	40.1	$CDCl_3$
SAT^D (9, X = NSO_2Ph)	56.4			33.3				$CDCl_3$
DIENE (6, X = NCO_2Me)	57.2	137.8	108.5	36.4	121.7	122.2	36.4	$CDCl_3$
Δ^3-ENE (7, X = NCO_2Me)	$54.3^{\ddagger}$	$123.1^{\ddagger}$	$113.8^{\ddagger}$	35.1			33.5	$CDCl_3$
Δ^6-ENE (8, X = NCO_2Me)	56.4			38.3	137.1	127.9	38.1	$CDCl_3$
SAT^D (9, X = NCO_2Me)	54.1			33.8				$CDCl_3$
DIENE (6, X = NBu^t)	45.0	136.2	116.5		134.2	125.0		$CDCl_3$
Δ^3-ENE (7, X = NMe)	59.5	134.3	107.6					$CDCl_3$ - 60°C
Δ^6-ENE (8, X = NMe)	63.6			37.1	135.9	124.7		$CDCl_3$ - 40°C
Δ^6-ENE (8, X = NH)	57.2			38.2	135.6	127.6		$CDCl_3$
SAT^D (9, X = NBu^t)	49.9			38.0				CCl_4
DIENE (6, X = S)	45.0	129.5	117.6	36.8	120.6	120.6	34.5	$CDCl_3$
Δ^3-ENE (7, X = S)	77.0	128.3	117.3	40.2				$CDCl_3$
SAT^D (9, X = S)	40.3			35.1				$CDCl_3$

‡ averaged over both geometrical isomers

Other assignments were made by analogy and were in keeping with the multiplicities observed.

^{13}C-Shielding and deshielding effects on the olefinic carbons on conversion of the monoenes to the dienes seemed largest at C_3 and C_6 for the dienes (6, X = NSO_2Ph and 6, X = NCO_2Me). This *may* denote a homoconjugative effect but, looking at Table 2 as a whole, the trend is not that expected from the availability of the lone pairs for conjugation and so some other explanation may be indicated.

Photoelectron spectroscopy. One of the most direct methods of measuring the interaction of non-conjugated π-systems in ground state molecules is to examine the difference in the ionisation potentials of the interacting double bonds relative to the "parent" interacting systems.[24] Although trishomoaromaticity is claimed to be manifest in the PE spectrum of the triene 3,[9] the neutral carbocyclic analogue 12 of the 2 - heterobicyclo[3.2.1]octa - 3,6 - dienes had a PE spectrum[9] which was essentially a superposition of the spectra of norbornene 13 and cyclohepta - 1,3 - diene 14. We have summarised the PE spectra of the dienes 6 and their derivatives in Table 3, again noting that the ^{1}H NMR spectra of the more unstable compounds showed them to be pure *after* running the PE spectrum. Our values for the 3-ene (7, X = NMe) are in fair agreement with the literature,[25] and although we could not obtain a good spectrum of the unstable diene (6, X = NMe), two of its ionisation potentials have been published[25] and we have used these here.

In the oxa-series, the PE spectrum of the diene (6, X = O) seems very close to a superposition of the spectra of the 3-ene (7, X = O) and of norbornene 13. In the aza-series, the nitrogen lone pair is destabilised on insertion of the Δ^3-π bond in the saturated compound (0.54 eV for (7, X = NSO_2Ph), 0.67 eV for (7, X = NCO_2Me) and 0.94 eV for (7, X = N-alkyl)). This is expected for an enamine system, a cyclopentenamine lone pair being destabilised by 0.88 eV[26] and a cyclohexenamine lone pair by 0.53 eV.[26] There are much smaller changes in the ionisation potentials of the lone pairs or of the Δ^6-π orbitals on comparing either (a) the saturated analogues 9 with the 6-enes 8 or (b) the 3-enes

Table 3. Photoelectron spectra of 2-heterobicyclo[3.2.1]octanes, enes and dienes

COMPOUND	IONISATION POTENTIALS (eV)		
	n_X	$\Delta^6\pi$	$\Delta^3\pi$
DIENE (6, X = O)	8.04–8.24 8.42	9.0	10.66
Δ^3-ENE (7, X = O)	8.01–8.18 8.38		10.66
NORBORNENE (13)		8.95	
DIENE (6, X = NSO_2Ph)	8.11	9.64	10.84
Δ^3-ENE (7, X = NSO_2Ph)	8.18		10.82
Δ^6-ENE (8, X = NSO_2Ph)	8.79	9.67	
SAT^D (9, X = NSO_2Ph)	8.72		
DIENE (6, X = NCO_2Me)	8.20	9.45 ‡	10.95
Δ^3-ENE (7, X = NCO_2Me)	8.03		10.99
Δ^6-ENE (8, X = NCO_2Me)	8.60	9.48 ‡	
SAT^D (9, X = NCO_2Me)	8.70		
DIENE (6, X = NBu^t)	7.06	8.85	9.93
DIENE (6, X = NMe)	7.28		10.17
Δ^3-ENE (7, X = NMe)	7.36		10.04
Δ^6-ENE (8, X = NH)	8.60	9.30	
Δ^6-ENE (8, X = NMe)	8.18	9.25	
SAT^D (9, X = Bu^t)	8.30		
DIENE (6, X = S)	8.03–8.12	9.13	10.50
Δ^3-ENE (7, X = S)	7.92		10.50
SAT^D (9, X = S)	8.43–8.52		

‡ Overlapping with bands attributed to the phenyl group.

7 with the dienes **6**. The effects are of the order found for homoallylic interactions[27] and there would seem to be little evidence for any special effect due to the 6 π-electron system in the dienes **6**. Comparisons in the N-alkyl series unfortunately had to be made between compounds with different alkyl groups and so the apparently larger destabilisation of the Δ^6-π orbital here should be treated with caution. In the thia-series there is an obvious thioenolether conjugation but such figures as we have suggest little more than this.

Addition of TCNE to the dienes **6**. It is well known that tetracyanoethylene (TCNE) undergoes non-concerted ionic thermal 2 + 2 cycloaddition reactions with electron-rich olefins,[28] and that norbornadiene undergoes a 4 + 2 cycloaddition with TCNE to give a "homo" Diels–Alder adduct **15**.[29] We were therefore interested to see which course the reaction of the dienes **6** with TCNE would take. 2 - Oxabicyclo[3.2.1]octa - 3,6 - diene (**6**, X = O) was known[30] to yield the [2 + 2]-adduct (**16**, X = O) but, when we attempted this reaction with the 4-methyl,[31] and 4-chloro[32] derivatives of this diene, no product was obtained under conditions which yielded us the adduct (**16**, X = O). It is known[28] that [2 + 2]-additions of TCNE with vinyl ethers is subject to steric retardation by β-substituents but when we had such substituents, [4 + 2]-addition did not replace [2 + 2]-addition. The reaction of TCNE with the dienes (**6**, X = NSO_2Ph, NCO_2Me and NCN) gave the unmistakable product **16** of 2 + 2 cyclo-addition. Reaction with (**6**, X = NMe) gave a product with no olefinic protons in the ^1H NMR spectrum but unfortunately neither this compound nor adducts of further dienes **6** could be characterised fully. The diene (**6**, X = CH_2) gave no adduct under the conditions used.

EXPERIMENTAL

^1H NMR spectra were recorded on Varian HA 100. Perkin-Elmer R32 or Varian and Perkin-Elmer 220 MHz instruments using TMS as an internal standard. We thank PCMU, Harwell for the 220 MHz spectra. ^{13}C NMR spectra were recorded on a Jeol PFT 100 instrument at 25.1493 Hz using TMS as an internal standard. We thank Mr. T. M. Siverns for these spectra. Photoelectron spectra were recorded on a Perkin-Elmer PS16 instrument with a modified high intensity lamp. Mass spectra were taken on an AEI MS9 instrument by Mr. A. Greenway and the microanalysis was performed by Mr. and Mrs. A. G. Olney.

Cycloadditions of the dienes 5 *with* TCNE. Equimolecular amounts of TCNE and diene **6** at a concentration of *ca.* 500 mg TCNE per 25 ml benzene gave a solution which invariably developed an intense colour; the adduct precipitated from solution and was filtered and washed with benzene and dried *in vacuo*.

(a) *The norbornadiene adduct* **15** was obtained after 8 days in 71% yield, m.p. 184–186° (lit.[29] 186–188°), $\tau((CD_3)_2C{=}O)$ 6.90 (2 H, s, H_2 and H_4), 7.32 (1 H, br s, H_1), 8.02 (2 H, s, H_7), 8.26 (3 H, m, H_3, H_4 and H_5). (b) *The* 2 - *oxabicyclo*[3.2.1]*octa* - 3,6 - *diene adduct* (**16**, X = O) had the expected[30] spectra and properties. (c) *The* N *phenylsulphonyl* - 2 - *azabicyclo*[3.2.1]*octa* - 3,6 - *diene adduct* (**16**, X = NSO_2Ph) was obtained after 5 days in 43% yield (Found: C, 61.1; H, 3.8; N, 18.4. $C_{19}H_{13}N_5SO_2$ requires: C, 60.8; H, 3.5; N, 18.7%), τ $((CD_3)_2CO)$ 2.21 (5 H, m, aromatics), 3.92 (1 H, d Xd, J 6 Hz and 3 Hz H_9), 4.32 (1 H, dxd, J 6 Hz and 3 Hz, H_8), 4.60 (1 H, d J 11 Hz, H_3), 5.22 (1 H, m, H_1), 6.0 (1 H, d, J 11 Hz, H_4), 6.76 (1 H, m, H_7), 7.38 (1 H, d, J 14 Hz, H_{10a}), 7.62 (1 H, txd, J 14 Hz and 4 Hz, H_{10s}). (d) *The* N - *carbomethoxy* - 2 - *azabicyclo*[3.2.1]*octa*-3,6 - *diene adduct* (**16**, X = NCO_2Me) was obtained after 3 days in 64% yield, *m/e* 293 (M^+), τ $((CD_3)_2CO)$ 3.72 (2 H, s, H_8 and H_9), 4.70 (1 H, d, J 10 Hz, H_3) 5.08 (1 H, m, H_1), 5.92 (1 H, m, H_4), 6.36 (3 H, s, CO_2Me), 6.74 (1 H, m, H_7), 7.60 (2 H, m, H_{10}). (e) *The* N - *cyano* - 2 - *azabicyclo*[3.2.1]*octa* - 3,6 - *diene adduct* (**16**, X = NCN) was obtained after 3 weeks in 6% yield (Found: *m/e* 260.07958. $C_{14}H_8N_6$ requires: 260.08104), τ $((CD_3)_2CO)$ 3.50 (2 H, AB, H_8 and H_9), 4.58 (1 H, d, J 10 Hz, H_3), 5.49 (1 H, br s, H_1), 5.82 (1 H, dxt, J 10 Hz and 1.5 Hz, H_4), 6.63 (1 H, m, H_7), 7.26 (1 H, d, J 14 Hz, H_{10a}), 7.56 (1 H, dxt, J 14 Hz and 4 Hz, H_{10s}).

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