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The Electronic Structures of Some Tetrazaborolines and Dimethyltetrazadieneirontricarbonyl

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Self-consistent field calculations have been performed on some Δ^2 tetrazaborolines using both an *ab initio* and a semi-empirical (CNDO) approach. The first method was employed in order to examine completely the ground-state and the properties of the π-electrons in the parent molecule. The excited states of several boron-substituted derivatives of tetrazaboroline have also been calculated semi-empirically, including configuration interaction, and good agreement with the observed electronic absorption spectra was obtained. The results of the calculations were also invoked to distinguish between isomeric boron-substituted derivatives of tetrazaborolines. The electronic structures of two of the possible geometries of dimethyltetrazadieneirontricarbonyl, in which the N_4 moiety is attached in a 'σ' or a 'π' fashion were examined by CNDO calculations and it was found that the more stable form involves σ bonding between the nitrogens and the iron atom.

Für einige Δ^2-tetrazaborwasserstoff-Derivate wurden SCF-Rechnungen nach einem *ab initio*- und nach einem semiempirischen (CNDO)-Verfahren durchgeführt. Die erste Methode wurde angewandt, um den Grundzustand und die Eigenschaften der π-Elektronen im Ausgangsmolekül zu untersuchen. Die angeregten Zustände einiger am Boratom substituierter Derivate wurden semiempirisch unter Einschluß von Konfigurationenwechselwirkung berechnet, wobei gute Übereinstimmung mit den experimentellen Elektronenspektren erzielt wurde. Die Resultate wurden ebenfalls zur Unterscheidung verschiedener isomerer Derivate benutzt. Die Elektronenstruktur von zwei möglichen Geometrien des Dimethyltetrazadieneisentricarbonyl, in denen der N_4-Rest mit einer σ- oder π-Bindung gebunden ist, wurde mit CNDO-Rechnungen untersucht. Es wurde gefunden, daß die stabilere Form σ-Bindungen zwischen den Stickstoffatomen und dem Eisenatom enthält.

Introduction

An interesting series of compounds which have been synthesised in the last decade are the stable Δ^2 tetrazaborolines [7, 11]. The geometry of the parent compound H_2N_4BH (Fig. 1a) is a planar five-membered ring [5]. An intriguing feature of these compounds is the presence of four nitrogens bonded together as a stable N_4 unit: such a system would normally be expected to decompose rapidly, yielding molecular nitrogen.

A compound which is formally related to tetrazaboroline is dimethyltetrazadieneirontricarbonyl [10] and this is of particular interest on account of the two plausible possible configurations which it could have. The first configuration (Fig. 2a) is the "π complex" in which the tetrazadiene moiety lies above the pyramidal $Fe(CO)_3$ group, the nitrogen atoms being non-coplanar with the iron atom. This structure is similar to the isoelectronic compound butadieneirontricarbonyl [13] in which the bonding involves the π system of the butadiene molecule [16].

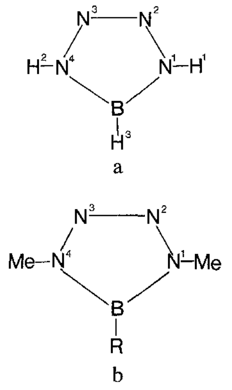

Fig. 1. Tetrazaboroline and substituted tetrazaborolines

In the second possible structure (Fig. 2b), the four nitrogen atoms are coplanar with the iron atom, the $Fe(CO)_3$ entity retaining its pyramidal configuration. The latter configuration is structurally related to the tetrazaboroline ring system and X-ray diffraction studies have shown that the compound does, indeed, have this geometry [6]. It seemed important, therefore, to try to rationalise (a) why the preferred configuration of the iron complex is the coplanar form, (b) how the bonding in this complex is related to that of the more conventional tetrazaboroline, and (c) the origin of the electronic absorption bands of the tetrazaborolines, and to correlate these with their detailed geometry.

Previous calculations carried out on various tetrazaborolines employed a simple iterative Hückel approach [14a] and concentrated attention on the six π electron system. The observed electronic absorption spectra were, therefore, interpreted solely in terms of $\pi \rightarrow \pi^*$ transitions. These previous calculations showed that, in all cases, there is a small drift of π electrons towards the boron atom, together with a large π bond order between nitrogen atoms 2 and 3. Weaker

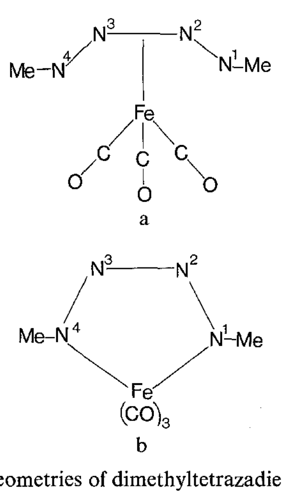

Fig. 2. Possible geometries of dimethyltetrazadieneirontricarbonyl

π bonds between nitrogens 1 and 2 and between nitrogens 1, 4 and boron were also revealed. As there seems to be only limited delocalisation of the π electrons in the system, then the reason for its stability could well be connected with the σ electrons. Hence, in order to try and establish these points with some degree of finality, we have carried through *ab initio* calculations on the ground-state of the parent compound H_2N_4BH together with CNDO-type all-valence electron calculations on selected compounds of the type Me_2N_4BR (Fig. 1b) so as to recalculate the excited states and, if necessary, to reassign the allowed bands.

The iron tricarbonyl complex contains too many atoms for an *ab initio* calculation to be feasible, and so here again we resorted to an all-valence electron CNDO method [1, 16, 17] to investigate the electronic structures of both configurations shown in Fig. 2. The geometrical parameters for the tetrazaboroline ring were taken from Ref. [5].

Results and Discussion

1. *Ab initio Calculations on Tetrazaboroline*

The calculational procedure assumed the LCAO MO SCF framework, the atomic orbital bases being linear combinations of gaussian-type orbitals [4]. The basis set comprised seven *s* and three *p* primitive gaussian orbitals contracted to three *s* and one *p* orbitals for the boron and nitrogen atoms and three *s* primitive gaussians [19] contracted to one atomic orbital for the hydrogen atom. The choice of this basis set was determined so as to be consistent and allow comparison with earlier calculations on borazine [2].

The results of a Mulliken population analysis [15] on tetrazaboroline are presented in Table 1. The figures indicate that the boron is positively charged (+0.475) and that this stems from a σ electron flow (0.950) to nitrogens 1 and 4, offset by a much smaller π-electrons drift (0.494) from these nitrogens to the boron. Nitrogen atoms 1 and 4 are highly negatively charged, due to electron movement from both the hydrogens and the boron atom. By contrast, nitrogen atoms 2 and 3 are virtually electrically neutral. The bond populations imply that the N_2—N_3 bond is almost 50% stronger than the N_1—N_2 bond. This difference in strength is due entirely to a large π-electron contribution to the former bond, whereas this facet of the bonding is weak in the latter. The π-electron system consists, therefore, of a partially delocalised six-electron arrangement in which the electrons are largely concentrated in the N_2—N_3 and the two N—B bonds. These results correspond largely with those of the previous "π only" calculations [14].

It is of interest to compare these results with those for borazine [2]. The gross atomic populations on the boron and the hydrogen atoms are very similar in both molecules but, as might be expected, differences arise in the charge which resides on the nitrogen atoms: those in borazine are more negatively charged than those in tetrazaboroline. The bond overlap populations found for borazine are B—H 0.446; N—H 0.364; and B—N 0.425; of which 0.327 is σ and 0.098 is of π type. These are all strikingly close to the corresponding quantities calculated in the present work for tetrazaboroline, especially those appertaining to the B—N bond.

Table 1. Mulliken population analysis of tetrazaboroline

Atom populations		Overlap populations		
Boron				
S	2.673	B—H		0.493
P_x	0.529	N—H		0.399
P_y	0.829			
P_z	0.494	B—$N_{1,4}$	σ	0.310
Total	4.525		π	0.117
			Total	0.427
Nitrogens 1, 4				
S	3.477	N_1—N_2	σ	0.271
P_x	1.339		π	0.041
P_y	1.120		Total	0.312
P_z	1.645			
Total	7.581	N_2—N_3	σ	0.294
			π	0.177
			Total	0.471
Nitrogens 2, 3				
S	3.628	N_1—N_4	σ	−0.109
P_x	1.087		π	−0.007
P_y	1.214		Total	−0.116
P_z	1.108			
Total	7.037			
Hydrogen 3				
	1.021			
Hydrogen 1, 2				
	0.609			

The B—H overlap populations in the two molecules can usefully be correlated with the observed B—H stretching frequencies, i.e., $\nu_{B-H} = 2627\,\mathrm{cm}^{-1}$ and $2530\,\mathrm{cm}^{-1}$ for dimethyltetrazaboroline [11b] and borazine respectively [18]. It seems, then, that the stability of the tetrazaboroline system can be, in part, attributed to the B—N bonds therein, since these are of similar strength to those in the stable molecule borazine.

The total and orbital energies of tetrazaboroline are given in Table 2. The highest filled orbital is of π-type and is equally distributed over the atoms. Its energy predicts an ionisation potential of 11.9 eV which can be compared with the experimental value of 10.4 eV for Me_2N_4BH [14b]. The first virtual orbital is also of π-symmetry but, surprisingly, contains no contribution from the boron π-orbital. In fact, it is the second virtual orbital (also of π type) which is largely concentrated on boron. This is the first example of a planar compound containing boron whose first π-type virtual orbital is *not* concentrated on the boron atom, and the implications of this are deeply significant. This finding explains why the boron atom in tetrazaboroline exhibits no acceptor properties and it also leads to the revolutionary suggestion that the compound could perhaps form complexes

Table 2. The total and orbital energies of tetrazaboroline (a.u.)

(a) Delocalised model	(b) Localised model
Electronic energy	
-407.0372	-406.9384
Nuclear energy	
163.5349	163.5349
Total energy	
-243.5023	-243.4035
0.155 (b_2) π	
0.132 (a_2) π	
$-$ 0.439 (b_2) π	
$-$ 0.491 (b_1)	
$-$ 0.529 (a_2) π	
$-$ 0.551 (a_1)	
$-$ 0.618 (a_1)	
$-$ 0.697 (b_2) π	
$-$ 0.708 (b_1)	
$-$ 0.782 (a_1)	
$-$ 0.892 (a_1)	
$-$ 0.911 (b_1)	
$-$ 1.188 (a_1)	
$-$ 1.292 (b_1)	
$-$ 1.518 (a_1)	
$-$ 7.818 (a_1)	
$-$ 15.699 (b_1)	
$-$ 15.699 (a_1)	
$-$ 15.744 (a_1)	
$-$ 15.745 (b_1)	

with electron donors in which the nitrogen atoms 2 and 3 would function as *acceptor* sites. This somewhat startling conclusion may also afford an explanation of why these cyclic compounds behave so curiously with known electron acceptors: thus with BCl_3 a simple 1:1 complex is formed but, with electron acceptors containing atoms which can act as electron donors, e. g., the chlorine atoms in Al_2Cl_6, $GaCl_3$, and $TiCl_4$, then ill-defined compounds or adducts with unusual stoicheiometry are produced [8]. It is clear that a completely new approach to the structural chemistry of the complexes formed by this "ligand" must be adopted.

In order to estimate the π-delocalisation energy of the N—B—N section of the molecule, the *ab initio* calculation was repeated with the π orbital of the boron atom excluded. Some of the results of this calculation are also given in Table 2. From the total energies, the π-delocalisation energy of the molecule is calculated to 61.9 kJ mol^{-1}. By comparison, the π-delocalisation energy of borazine is 119.1 kJ mol^{-1}. In the latter case this amounts to some 80 kJ per bond, whereas for the tetrazaboroline the corresponding quantity is ~130 kJ per bond. Although it is recognised that the molecules are not strictly comparable, these figures do indicate that the π-stabilisation energy is substantial for tetrazaboroline.

2. *All-Valence Electron Calculations on the Excited States of* Me_2N_4B—X *Derivatives*

In this section of the work, a series of compounds of the type Me_2N_4BR (Fig. 1b) was examined theoretically in order to discover details of the nature of the excited states of the systems and the effects of the substituents R on the ring states and electronic spectra. Of these, the derivatives formed in the following way are particularly interesting: when the B-halogeno compounds are treated with silver cyanide or silver thiocyanate, as might be expected, the pseudohalogen replaces the halogen atom. However, infra-red and Raman spectroscopy have been unable to establish whether the products contain the normal or *iso* pseudohalogen groups [12].

In this series of calculations, a common geometry was assumed for the tetrazaboroline moiety. The bond lengths and angles were abstracted from the recent work of Bauer [5]. The geometries assumed for the B—R group are detailed in Table 3 and for the vinyl derivative two isomers were studied, in which the vinyl group was positioned parallel or perpendicular to the N_4B ring plane. The excited states were obtained by considering one-electron excitations forming a specified set of σ- and π-based configurations. Interaction between all the excited configurations was included in the usual way. The result of this treatment, together with the observed absorption bands of the compounds, are presented in Table 4. The experimental data are taken mainly from the work of Leach and Morris [11, 12].

Table 3. Bond lengths (n.m.) for substituents in boron substituted tetrazaborolines

Substituent	Bond lengths		
R			
—CH_3, —C_2H_3	B—C, 0.154;	C—C, 0.135[a]	
—CN	B—C, 0.154;	C—N, 0.1157[a]	
—NC	B—N, 0.142;	N—C, 0.1167[a]	
—SCN	B—S, 0.161;	S—C, 0.161;	C—N, 0.121[a]
—NCS	B—N, 0.142;	N—C, 0.122;	C—S, 0.156[a]

[a] Ref. [9].

Of the two vinyl compounds, the "perpendicular" isomer has the lowest total energy: we shall, therefore, restrict discussion to this derivative and only results appertaining to it are given in Table 4.

When (a) chlorine, (b) vinyl, and (c) hydrogen are the substituents on boron, the agreement between the observed and calculated electronic transition energies is good. In general, the low-energy non-allowed transitions are all of $\sigma-\pi^*$ type and these states resemble those calculated for the vinyl boranes [3].

As a more detailed illustration, we will consider the calculated spectrum of the chloro derivative: the spectra of the other compounds are closely related to this case.

Table 4. Electronic state energies (eV) of some boron-substituted tetrazaborolines

		$E_{\text{calc.}}$	$f_{\text{calc.}}$	$E_{\text{expt.}}$		$E_{\text{calc.}}$	$f_{\text{calc.}}$	$E_{\text{expt.}}$
(a) R = Cl	$^1\Psi_1$	4.25	0.00		(b) R = H	3.81	0.00	
	$^1\Psi_2$	4.39	0.00			4.28	0.00	
	$^1\Psi_3$	5.07	0.00			5.62	0.02	
	$^1\Psi_4$	5.68	0.09	5.79		6.25	0.05	6.26
	$^1\Psi_5$	6.62	0.00			6.41	0.00	
(c) R = —CH=CH$_2$	$^1\Psi_1$	3.43	0.00					
	$^1\Psi_2$	3.97	0.00					
	$^1\Psi_3$	4.21	0.00					
	$^1\Psi_4$	4.72	0.00					
	$^1\Psi_5$	5.41	0.99	5.77				
	$^1\Psi_6$	6.11	0.03					
(d) R = —SCN	$^1\Psi_1$	4.23	0.00		(e) R = —NCS	4.13	0.00	
	$^1\Psi_2$	4.30	0.00			4.29	0.00	
	$^1\Psi_3$	5.09	0.00			4.53	0.00	
	$^1\Psi_4$	5.57	0.10			4.57	0.04	4.84(sh.)
	$^1\Psi_5$	5.84	0.00			4.79	0.00	
	$^1\Psi_6$	6.10	0.00			5.52	0.00	
	$^1\Psi_7$	6.12	0.05			6.01	0.28	6.11
	$^1\Psi_8$	6.56	0.00			6.26	0.00	
(f) R = —CN	$^1\Psi_1$	4.12	0.00		(g) R = —NC	4.27	0.00	
	$^1\Psi_2$	4.13	0.00			4.31	0.00	
	$^1\Psi_3$	4.76	0.00			4.59	0.00	
	$^1\Psi_4$	5.06	0.00			4.77	0.00	
	$^1\Psi_5$	5.34	0.00			5.28	0.00	
	$^1\Psi_6$	5.44	0.07			5.83	0.07	
	$^1\Psi_7$	6.48	0.04	6.20		6.70	0.02	

The first calculated band stems from a $\sigma-\pi^*$ transition, of which the main contributing configuration is an excitation from a $p_\sigma - p_\sigma$ bond between the inner nitrogens to a π^* orbital situated mainly on the two inner nitrogen atoms. The second and third bands are also of $\sigma-\pi^*$ character. The first $\pi-\pi^*$ transition gives rise to the observed spectrum and occurs from a π-orbital which is evenly distributed about the boron and nitrogen atoms. The excited π^* orbital here is that appertaining to the B—Cl bond.

From the calculated excited states of the thiocyanate and isothiocyanate derivatives, it can be seen that better agreement with the observed spectra is obtained from the isothiocyanate. The allowed transitions are $\pi-\pi^*$ in nature and they are lower in energy than the corresponding states in compounds (a–c). The total valence energies obtained from the calculations are not *absolutely* meaningful but do indicate that the isothiocyanate is to be energetically preferred over the thiocyanate derivative.

Charge Distribution in Tetrazaborolines

The data relating to the distribution of charge over the series of molecules are given in Table 5. The atoms may be identified by the generic numbering scheme in Fig. 3. The whole series reveals itself as one of remarkably non-polar compounds, particularly around the central ring.

The bonding in the "normal" and *iso* thiocyanate groups in these compounds proves to be very interesting. The classical formulation of the bonds is —S—C≡N and —N=C=S, whereas the data in Table 6 reveal that there is, in each case, a strong bonding component between the sulphur and nitrogen atoms which is mainly of π type. This is a most uncommon feature and arises because the "bonding power" of the sulphur atom is markedly increased by 3*d* orbital participation in the π system of the group.

Table 5. Charge distribution in substituted tetrazaborolines, Me_4N_4BR

Substituent R	—C_2H_3	—Cl	H	—CN	—NC	CH_3	—NCS	—SCN
B	+0.11	+0.17	−0.10	+0.02	+0.13	+0.15	+0.15	+0.11
N_1	−0.06	−0.04	−0.00	−0.02	−0.05	−0.08	−0.06	−0.07
N_2	−0.05	−0.04	−0.05	−0.05	−0.04	−0.06	−0.04	−0.04
C_1	−0.18	−0.16	−0.17	−0.17	−0.17	−0.18	−0.17	−0.18
H_1	+0.09	+0.10	+0.09	+0.09	+0.09	+0.08	+0.09	+0.09
H_2	+0.08	+0.10	+0.09	+0.09	+0.09	+0.08	+0.09	+0.09
H_3	+0.09	+0.10	+0.09	+0.09	+0.09	+0.08	+0.09	+0.09
X_1	−0.14	−0.28	+0.01	−0.02	−0.03	−0.38	−0.15	+0.01
X_2	−0.15	—	—	−0.08	−0.13	—	+0.25	+0.08
X_3	—	—	—	—	—	—	−0.25	−0.16
H_4	+0.09	—	—	—	—	+0.11	—	–
H_5, H_6	+0.07	—	—	—	—	—	—	—

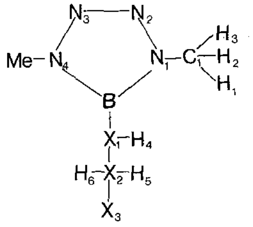

Fig. 3. Key to numbering for charge distribution in substituted tetrazaborolines

Table 6. Bond orders in the —N—C—S and —S—C—N groups

π	N—C	1.048	π	C—N	1.575
	C—S	0.795		S—C	0.406
	N—S	0.407		S—N	0.307
$\sigma+\pi$	N—C	2.017	$\sigma+\pi$	C—N	2.548
	C—S	1.820		S—C	1.404
	N—S	0.444		S—N	0.350

3. *All-Valence Electron Calculations on* $Me_2N_4Fe(CO)_3$

The same calculational procedures with the same parametrisation as in previous calculations [16] on butadieneirontricarbonyl were employed to examine dimethyltetrazadiene and its complex with iron tricarbonyl. The geometry of the σ complex was taken from recent crystallographic work [6]. That of the π-complex was assumed to be broadly similar to that of butadieneirontricarbonyl [13] (see Fig. 2). The dimethyltetrazadiene moiety was positioned in a plane above and perpendicular to a pyramidal $Fe(CO)_3$ group. The bond lengths and angles within the separate dimethyltetrazadiene and iron tricarbonyl units were the same as in the σ complex. The Fe—N_1,N_4 and Fe—N_2,N_3 bond distances were taken to be equal to that of the Fe—N_1 distance in the known complex: the tetrazadiene plane was hence situated at a distance 0.161 nm from the iron atom.

In this problem we are concerned with determining the minimum energy configuration and, hence, the total valence electronic energy, and the charge distribution for the two structures shown in Fig. 2 are presented in Table 7. It can immediately be seen that the order of total energies for the structures confirms the crystallographic result [6] that the σ-bonded structure (Fig. 2b) is the more stable of the two.

The electron population distribution shows that, in the σ-complex, there is, overall, a limited movement of electrons to the iron tricarbonyl unit: this comprises a π-electron drift (0.50) towards the iron tricarbonyl unit, coupled with a σ-electron (0.46) polarisation towards the complexed dienoid moiety. Examina-

Table 7. Electronic energies (eV) and charge distributions for the "σ"- and "π"-structures of dimethyltetrazadieneirontricarbonyl

	σ-complex		π-complex	
Electronic energy	−15693.9		−15804.9	
Nuclear energy	12114.9		12239.2	
Total energy	− 3579.0		− 3565.7	
Electronic density				
Iron				
4*s*	0.44		0.44	
4*p*	0.87		0.88	
3*d*	7.21		7.25	
Total	8.52		8.57	
Nitrogen (N_1) σ	3.38		3.86	
π	1.61		1.17	
Total	4.99		5.03	
Nitrogen (N_2) σ	3.91		3.92	
π	1.14		1.03	
Total	5.05		4.95	
Carbon (methyl)	4.29		4.19	
Carbon (carbonyl)	3.77[a]	3.85	3.85[a]	3.82
Oxygen	6.07[a]	5.99	5.97[a]	6.07
Hydrogen	0.92[a]	0.89	0.92[a]	0.90

[a] Unique carbonyl group and hydrogen atom.

tion of the electron densities of the Me_2N_4 unit before and after complexing reveals that π-electrons are evenly supplied from both the inner (0.10) and outer (0.15) nitrogens. The σ-electron distribution is interesting as the "extra" electron density from the $Fe(CO)_3$ unit is distributed throughout the σ-electron system of Me_2N_4, with a bias towards the inner nitrogens. One overall result of this two-way electron flow is to reduce the electron density on the outer nitrogens and to increase the electron density on the inner nitrogens, i. e., complex formation tends therefore to equalise the electron density over the nitrogen atoms. The iron is negatively charged (0.51) and most of this (0.48) originates from the tricarbonyl moiety. The iron charge stems from σ donation of electrons which originate from the s and p_σ orbitals of the carbonyl carbon. A modicum of π-back donation from iron to the CO moieties is also evident. The result of the latter charge movement is to alter the electron distribution on both C and O as compared with free carbon monoxide calculated by the same method. Thus, the charge on carbon is altered from -0.15 to $+0.23$ and that on oxygen changes from $+0.15$ to -0.17. The σ-donation thus reduces the carbon density and the π-back donation increases the oxygen population. A comparison of the bond order data shows that there is a small decrease in all the nitrogen-nitrogen bond orders on complexing but that the σ bonds formed between the iron and the outer nitrogens are strong (bond order, 0.41). Furthermore, in the tetrazadiene moiety, the "π" (i. e., those antisymmetric to the N_4H_2 plane) contain 5.50 electrons and so, together with the "π" orbitals on the iron, form a six-π-electron ring system similar in nature to that of the tetrazaborolines. The stability of the complex results from this factor and the strong bonding between Fe and N_1, N_4.

The electron distribution in the π complexed structure is, overall, rather similar to that of the σ complex. The most significant difference occurs in the π electron population of the nitrogen atoms, being 4.40, and 5.50 for the π and σ complexes respectively. The bond orders in the π complex show that the iron atom forms bonds to both the inner (0.20) and the outer (0.26) nitrogen atoms. This electron-withdrawing process reduces the π electron population of all the nitrogens but leaves the σ orbitals of the outer pair essentially unchanged, and the iron has appreciable bond orders only with the outer nitrogens (0.41).

4. *The Electronic Structures of Tetrazadiene and Butadiene*

Although tetrazadiene (N_4H_2) and butadiene are isoelectronic systems, they form different types of complex with the iron tricarbonyl group. It is not surprising that the latter does not yield an adduct which is σ bonded from the terminal carbons, since this would (a) require prior rotation of the two end —CH_2 groups out of the plane of the molecule, and (b) cause disruption of the stable totally-symmeric all-spin-paired σ bonding situation in the molecule. However, it is interesting to enquire why the latter does not apply equally to tetrazadiene (the former reason is clearly not relevant) and hence we also carried through Gaussian calculations with limited basis sets on the two ligands.

The orbital energy levels are presented in Table 8 and show several interesting features. Firstly, in both cases there are only two filled π orbitals. Secondly, in

Table 8. The energy levels of butadiene and tetrazadiene

Butadiene	Tetrazadiene
0.372 (a_1)	0.412 (a_1)
0.227 (a_2) π	0.177 (a_2) π
0.055 (b_2) π	0.010 (b_2) π
$-$ 0.403 (a_2) π	$-$ 0.407 (b_1)
$-$ 0.529 (b_2) π	$-$ 0.426 (a_2) π
$-$ 0.571 (a_1)	$-$ 0.486 (a_1)
$-$ 0.575 (b_1)	$-$ 0.554 (b_1)
$-$ 0.636 (b_1)	$-$ 0.622 (b_2) π
$-$ 0.671 (a_1)	$-$ 0.665 (a_1)
$-$ 0.743 (a_1)	$-$ 0.770 (a_1)
$-$ 0.781 (b_1)	$-$ 0.871 (b_1)
$-$ 0.905 (a_1)	$-$ 1.115 (a_1)
$-$ 1.062 (b_1)	$-$ 1.262 (b_1)
$-$ 1.176 (a_1)	$-$ 1.480 (a_1)
$-$11.406 (a_1)	$-$15.675 (a_1)
$-$11.406 (b_1)	$-$15.675 (b_1)
$-$11.428 (a_1)	$-$15.744 (a_1)
$-$11.428 (b_1)	$-$15.745 (b_1)

tetrazadiene there is a low-lying vacant π-orbital which becomes occupied on σ bonding with the $Fe(CO)_3$ groups. This is an interesting feature and its occupancy represents a diversion of electron density from σ-type orbitals to those of π type in the final complex. This orbital thus brings about the stable six-π-electron ring. The highest filled orbital of tetrazadiene is of σ type (b_1 symmetry) and it is built from a linear combination of orbitals situated on the outer nitrogens. This orbital helps bring about the important $Fe—N_1$ σ bonds.

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