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An original route to newly-functionalized indoles and carbazoles starting from the ring-opening of nitrothiophenes

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ABSTRACT

The multifaceted behavior of nitrobutadienes deriving from the initial ring-opening of nitrothiophenes finds a further clear-cut example in their Michael-type acceptor reactivity towards indole. Thus, depending on the starting diene, either newly-functionalized indoles or carbazoles are produced, the latter as the result of an appealing double (intermolecular + intramolecular) Michael-type addition to a nitrovinylic moiety. The outcome encompasses motifs for both mechanistic and synthetic interest in the field of heterocycles endowed with possible pharmacological activity.

The highly functionalized aminobutadienes **2**, **5,** and **9**, smoothly originating from the ring-opening of 3,4-dinitrothiophene **1**,[1] 3-nitrothiophene **4**[2] or 2-nitrothiophene **8**,[3] respectively, with secondary amines (Scheme 1), represent valuable building blocks in the field of organic synthesis.[4–21] In the last two decades we have reported a number of interesting applications of both the dinitro-[4–11] and nitro-butadienes[12–21] **3**, **6**, **7**, **10,** and **11**, which mainly exploit proper preliminary modifications of the functionalities deriving from the initial ring-opening.

In particular, within a multifaceted reactivity endowed with potentialities which cannot be offered by, for example, simple nitroalkenes,[22] a manifold production of homo- and heterocyclic derivatives[7,19] significantly widens the application field of such conjugated systems. In this context, the effectiveness of the intramolecular Michael-type addition to the nitrovinyl moiety has more recently led to interesting novel *S*-heterocycles,[15,20,21,23] thus providing new precursors to target molecules with potential pharmacological activity.

In order to widen their synthetic scope, we have now turned to the behavior of our nitro- and dinitro-butadienes as Michael-type acceptors in intermolecular conjugate additions,[24] and herein report on some particularly rewarding preliminary results stemming from the employment of the biologically ubiquitous[25] indole (**12**) as the electron-rich nucleophilic partner.

A preliminary screening of reported experimental conditions[26] for the nucleophilic addition of indole to nitroolefins, carried out on the non-symmetric diene **10a** (Ar = Ph), has provided the results reported in Table 1. When detected, the isolated product (Exp. 1 and 2) was structurally in agreement with the expected Michael-type adduct (Scheme 2, **13a**), obtained, due to the generation of two chiral carbons, as a ca. 1.5:1 mixture of diastereoisomers (each as a racemic couple), with retention of the original configuration of the remaining double bond.

As a matter of facts, **10a** did not prove to be in general very reactive, leading at most to low substrate conversions: most likely the electron-donor effect of sulfur counteracts the electron-withdrawing one of the nitro group, resulting in an overall poor reactivity of the double bond(s) of **10a** as Michael-acceptor(s). Nevertheless, on the grounds of results obtained with an 'unfavorable' model system, we decided to extend the conditions of Exp. 2[27] to **11a** (Ar = Ph) (Scheme 3), that is, to a substrate for which we would expect a reactivity increase, thanks to the concomitant favorable effects of NO_2 and SO_2Me on the electrophilicity of the C(2) and/or C(4) carbon atoms.

The system immediately appeared much more rewarding, leading, in the smooth conditions applied, to the disappearance of substrate (3.5 h) and allowing the isolation of a more than satisfactory yield (77%) of the expected **14a** (Scheme 3), again as a mixture (ca. 1:1) of diastereoisomers[27] and retention of the double bond configuration.

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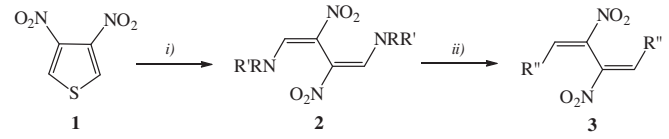
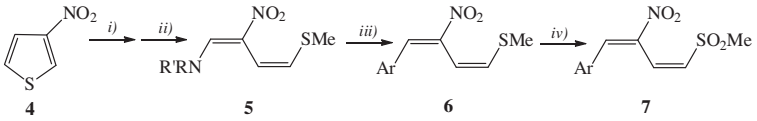
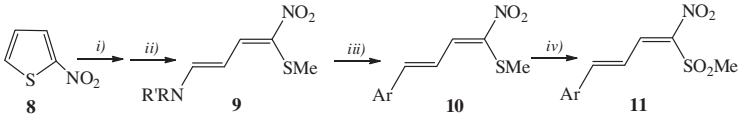


i) Et_2NH (excess), EtOH, 0 °C, overnight; *ii)* ArMgBr (2.2 mol equiv.), THF, 0 °C, 15'-45', then acidic quenching.



i) Pyrrolidine (2 mol equiv.), $AgNO_3$ (2 mol equiv.), EtOH, rt, overnight; *ii)* excess MeI, 0°C to rt, 2 h;
iii) ArMgBr (1.1 mol equiv.), THF, -78°C, 15–45 min., then acidic quenching; *iv)* MCPBA (2 mol equiv.), CH_2Cl_2, rt.



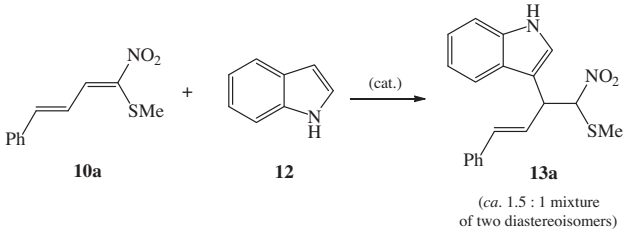
i) Pyrrolidine (9 mol equiv.), $AgNO_3$ (1 mol equiv.), EtOH, rt, overnight; *ii)* excess MeI, 0°C to rt, 2 h;
iii) ArMgBr (1.1 mol equiv.), THF, -30°C, 15–45 min., then acidic quenching; *iv)* MCPBA (2 mol equiv.), CH_2Cl_2, rt.

Scheme 1. Nitrobutadienic building-blocks from the ring-opening of nitrothiophenes **1**, **4**, **8**.

Table 1
Results from a preliminary screening of experimental conditions for the reaction between **10a** (Ar = Ph) and indole (**12**)

Exp.	**12** (mol equiv[a])	Catalyst (mol equiv[a])	Solvent	T (°C)	Time (days)	**10a** (recovered)	**13a**[b]
1	1.3	NBS (0.1)	CH_2Cl_2	40	5	80%	14%[c]
2	1	$Zn(OAc)_2$ (0.2)	EtOH	25	4	70%	21%[c]
3	4	I_2 (0.3)	Et_2O	25	4	100%	—
4	1	—	H_2O	Reflux	4	0%[d]	—
5	1	—	CF_3CH_2OH	25	4	ca. 100%	Traces

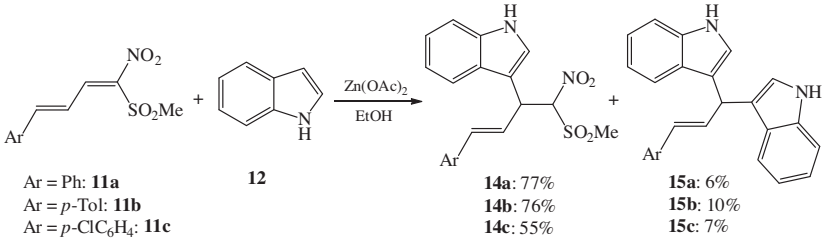
[a] With respect to **10a**.
[b] Ca. 1.5:1 diastereomeric mixture (see Ref. 27).
[c] Absolute yield.
[d] Extensive **10a** decomposition with no isolation of the expected product.



Scheme 2. Michael-type addition of indole to the nitrobutadiene from ring-opening of **8**.

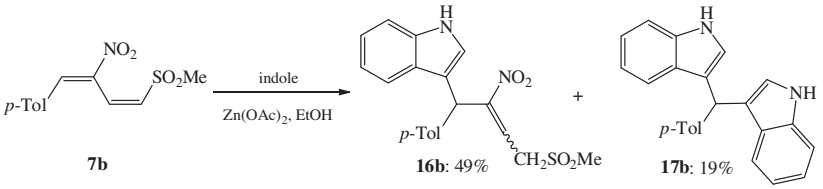
Moreover, interestingly enough, the main product was accompanied by small amounts (6%) of a secondary one whose structure, based on both ^1H and ^{13}C NMR analysis, corresponds to the bis(3-indolyl)methane derivative **15a**: replacement of a highly stabilized carbanion by indole from the main product can only be hypothesized at this stage. The formation of **15**, whose yield could conceivably be improved by a proper modulation of the reaction conditions, is surely not trivial, as it provides access to new examples of a class of bis(indolyl)-based molecules which are under investigation for their pharmacological/biological properties.[29,30] As shown in Scheme 3, very similar, rewarding results were obtained when extending the reaction to the *p*-tolyl (**11b**) and *p*-chlorophenyl (**11c**) derivatives, allowing to foresee a rather wide applicability range for our original approach.

In the context of our preliminary screening, butadienes **6** and **7**, deriving from the initial ring-opening of 3-nitrothiophene, issue different challenges, represented by (a) any propensity to react of the former (where an electronically unfavorable methylthio function is present, much alike **10**), or (b) the behavior of the latter, which holds good structural reasons for a regioselectivity issue relevant to the nucleophilic attack to either activated double bond.



Ar = Ph: **11a**
Ar = *p*-Tol: **11b**
Ar = *p*-ClC_6H_4: **11c**

Scheme 3. Products from the reaction between indole and nitrosulfonylbutadienes **11**.



7b

16b: 49% **17b**: 19%

Scheme 4. Products from the reaction between indole and nitrosulfonylbutadiene **7b**.

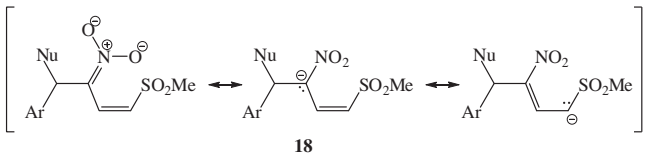
As a matter of facts, **6b** (Ar = *p*-Tol) showed, in ethanol, a very low reactivity at room temperature while yielding a very complex final mixture at 50 °C, most likely as the result of extensive decomposition.

On the other hand, the outcome of the reaction with **7b** (Scheme 4) was quite intriguing, whereby the main product **16b**, isolated after 24 h in a 49% yield as a ca. 4:1 *Z*:*E* mixture (as judged on the grounds of chemical shifts in the ^{1}H NMR spectrum),[27] is the result of a 1,4-addition to the dienic system: this requires that protonation of the delocalized anion **18** (Scheme 5), originated by selective nucleophilic addition to the nitrovinyl moiety, occurs at the carbon that binds the sulfonyl group rather than the nitro group.

The 1,4-addition is probably favored as it leads to a more substituted double bond and/or as it restores a thermodynamically stable nitrovinyl functionality: an outcome undoubtedly of particular interest from a synthetic point of view. As a matter of facts, we have already reported a similar outcome elsewhere.[15,20,21]

Besides to the main product, also in this case a bis(3-indolyl)methane derivative (**17b**)[27] was isolated: again, a nucleophilic displacement of a stabilized carbanion by a second molecule of indole is likely at play.

As far as dinitrobutadienes **3** are concerned, while structurally simpler because of their molecular symmetry, in our hands they have so far proved to be rather awkward and unpredictable systems, as reaction can affect just one nitrovinyl moiety[11] or both of them,[8,9,31] which could in turn behave independently[9] or cooperatively.[8,31] For the tests herein, we chose to use two molar equivalents of indole in order to cope with a foreseeable concurrent pathway represented by a double Michael addition.[8] Very first attempts also suggested mild heating (40 °C) and the use of non-catalytic amounts of zinc acetate in order to favor the reactivity.[32] Much to our surprise, starting from the bis(*p*-tolyl) derivative **3b** we could isolate, from a relatively complex final mixture, three different products, the two main ones being the isomeric nitrocarbazoles **19b** and **20b** (Scheme 6).



18

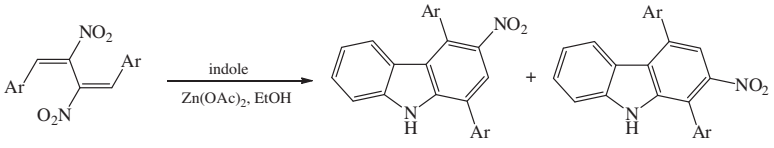
Scheme 5. Charge delocalization in the anionic intermediate **18**.

The unambiguous assignment of the 3-nitro-1,4-bis(*p*-tolyl)-9*H*-carbazole structure to **19b** was obtained by means of a single-crystal X-ray analysis after crystallization from ethanol, the relevant ORTEP drawing being reported in Figure 1.[33]

A reasonable mechanistic hypothesis, still awaiting experimental substantiation, is formulated in Scheme 7, where an initial, intermolecular, Michael addition to a nitrovinylic moiety to give **21** is followed by a second, intramolecular, nucleophilic attack onto the remaining nitrovinyl, again followed by restoration of the aromaticity of indole and eventually leading to the double addition product **22**: the neat result so far being a double electrophilic aromatic substitution at positions 3 and 2 of the indole nucleus, the diene acting as a double Michael acceptor and the indole as a double nucleophile. It is worth mentioning, at this regard, that, as recently reported in similar cases, a second participation of the indole nucleus as a nucleophile could involve the same C(3) position, to generate a *spiro*-type intermediate which would subsequently transform, in acidic media, into the final condensed system:[36] possibility which cannot be ruled out for our system, although not supported by any experimental data so far. As already noticed in previous studies of ours,[6,8] molecular arrays such as **22**, possessing two nitro groups on adjacent saturated carbon atoms, easily remove nitrous acid: in this case, given the nature of the tricyclic system, two different regioisomers can be originated, namely the intermediate cyclohexadiene derivatives **23** and **24**. Finally, via oxidation either by air or by the just released nitrous acid, both dienes could aromatize to the isolated carbazoles **19** and **20**.

Actually, so far we have not managed to obtain a suitable single crystal of the secondary product (i.e., **20**); nonetheless, the structure of 2-nitro-1,4-bis(*p*-tolyl)-9*H*-carbazole can be rather straightforwardly guessed on the grounds of the mechanistic hypothesis advanced. More reliable confirmation definitely comes from the spectral (^{1}H NMR, ^{13}C NMR, IR, UV–vis and GC–MS) analogies between **19b** and **20b**, as well as from some quantum mechanical calculations.

Surprisingly enough, the third (minor: 7%) product isolable from the reaction on **3b** is represented by the dinitrocarbazole **25b** (Scheme 8), whose identification again rests, at the moment, on spectroscopic evidences.[32] One must admit, in this case, a double oxidation of intermediate **22b**, strongly driven by the thermodynamic advantage of full aromatization, for which the system



Ar = Ph: **3a**
Ar = *p*-Tol: **3b**
Ar = *m*-ClC$_6$H$_4$: **3c**

19a: 48%
19b: 48%
19c: 29%

20a: 24%
20b: 27%
20c: 14%

Scheme 6. Isomeric nitrocarbazoles from the reaction between indole and dinitrobutadienes **3**.

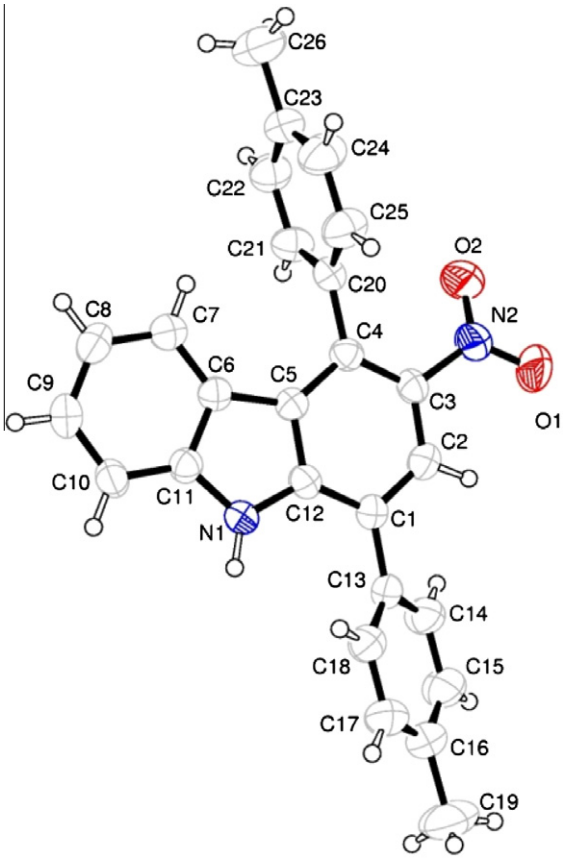
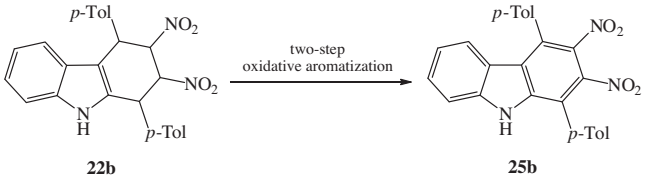


Figure 1. ORTEP drawing of carbazole **19b**. Ellipsoids enclose 50% probability.

most likely exploits the 'home-made' HNO_2 oxidant formed along the main pathway of Scheme 7.

On the grounds of the discussion above, the possibility to favor the formation of carbazoles by means of external oxidants has also been addressed. As a matter of fact, although the easy oxidability of indole itself heavily limits the use of an oxidant in the starting mixture, for the model **3b** we have preliminarily found that, in otherwise standard conditions,[32] the addition of DDQ after the standard reaction time (24 h) and before quenching with water actually increases the relative yield of the most oxidized product **25b** (Table 2). Optimization will presumably lead to even more enhanced selectivities.



Scheme 8. Oxidative pathway to dinitrocarbazole **25b**.

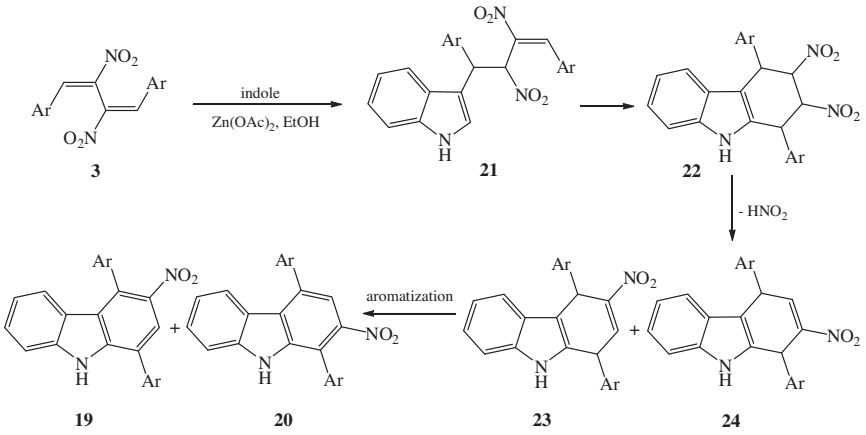
Table 2
Results for the reaction between **3b** and indole (**12**) in EtOH at 40 °C with or without added DDQ

Exp.	**12** (mol equiv[a])	DDQ (mol equiv[a])	Time (h)	**19b**[c]	**20b**[c]	**25b**[c]
1	2	—	24	48%	27%	7%
2	2	3	24 + 2[b]	31%		50%
3	2	5	24 + 2[b]	32%		49%

[a] With respect to **3b**.
[b] Additional time after DDQ addition, before water quenching.
[c] Absolute yield.

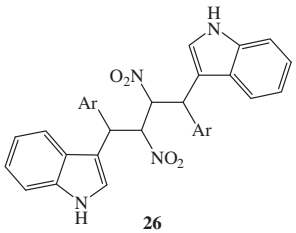
In conclusion, we feel that the preliminary results reported herein provide further valuable examples of the very interesting behavior, from the standpoint of both synthetic and mechanistic aspects, of the nitrosubstituted conjugated butadienes of Scheme 1. It is surely worth recalling that much interest is attached to the synthesis and/or functionalization of nitrogen heterocycles such as indoles[25] or carbazoles,[37] that is, molecules which, because of biological/pharmacological activity studies and/or technological applications, fill everyday's literature with papers and review articles.

Anyway, besides the general interest attached to the functionalized heterocycles obtained, it seems in particular worth noting that from the reaction on dinitrobutadienes **3** only carbazoles (**19**, **20** or **25**) could be isolated and identified: that is, products deriving from a double (intermolecular + intramolecular) Michael-type addition. Actually, the absence of substituted indoles deriving from a single intermolecular conjugate addition as well as of bis(3-indolyl)butanes deriving from a double intermolecular Michael addition (**26**) strongly suggests that **21**, initially formed by '*clipping*' of the 4-carbon chain onto indole, is 'forced' to cyclize most likely by a concomitance of structural, electronic, and/or geometric factors. On the other hand, the overall cyclization seems precluded (most likely for different reasons) to the systems of both Schemes 3 and 4, which could, at least in principle, build a five-member



Scheme 7. Proposed mechanism for the synthesis of nitrocarbazoles **19** and **20**.

carbon-ring fused to the indole heteroring, with no possibility, though, of complete aromatization.



26

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27. *Typical procedure for the reaction of nitrobutadienes **6**, **7**, **10** and **11** with indole:* To a stirred suspension of substrate (0.5 mmol) in ethanol (2.5 mL), indole (0.5 mmol) and zinc acetate (0.025 mmol) were added. The mixture was stirred at room temperature until the reaction was complete (TLC), the solvent was evaporated and the residue was purified by column chromatography using hexane/ethyl acetate (5:1) to collect **13** and hexane/ethyl acetate (3:1) to collect derivatives **14**–**17**.
*(E)-3-[1-(Methylthio)-1-nitro-4-phenylbut-3-en-2-yl]-1H-indole (**13a**):* isolated as a 1.5:1 mixture of diastereoisomers (A and B, respectively). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.17 (s, 3H of A), 2.30 (s, 3H of B), 4.52 (dd, J = 9.6, 7.8 Hz, 1H of A), 4.62 (dd, J = 9.8, 7.7 Hz, 1H of B), 5.77 (d, J = 9.9 Hz, 1H of B), 5.78 (d, J = 9.6 Hz, 1H of A), 6.49 (dd, J = 15.6, 7.7 Hz, 1H of B), 6.50 (dd, J = 15.6, 7.8 Hz, 1H of A), 6.59 (d, J = 15.7 Hz, 1H of A + 1H of B), 7.11–7.42 (m, 9H of A + 9H of B), 7.69 (d, J = 7.7 Hz, 1H of A + 1H of B), 8.15 (br s, 1H of B), 8.20 (br s, 1H of A). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 14.86, 15.26, 43.58, 44.06, 95.18, 96.07, 111.56, 111.70, 118.78, 118.91, 120.05, 120.10, 122.35, 122.59, 122.61, 122.64, 125.38, 125.64, 125.89, 126.51, 126.59, 127.82, 127.88, 128.40, 128.49, 128.53, 128.76, 133.40, 133.54, 136.24, 136.29, 136.45 (two pairs of carbons are accidentally isochronous).
*(E)-3-(1-(Methylsulfonyl)-1-nitro-4-(p-tolyl)but-3-en-2-yl)-1H-indole (**14b**):* isolated as ca. 1:1 mixture of diastereoisomers; two series of signals are present in the NMR spectra, although no assignment to either diastereoisomer is, at the moment, possible. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.31 (s, 6H), 2.67 (s, 3H), 3.16 (s, 3H), 4.91 (dd, J = 8.4, 10.5 Hz, 1H), 4.93 (t, J = 8.9 Hz, 1H), 5.95 (d, J = 10.0 Hz, 1H), 5.98 (d, J = 8.8 Hz, 1H), 6.44 (dd, J = 15.5, 8.6 Hz, 1H), 6.54 (dd, J = 15.6, 8.4 Hz, 1H), 6.65 (d, J = 10.1 Hz, 1H), 6.68 (d, J = 15.6 Hz, 1H), 7.10 (d, J = 7.8 Hz, 4H), 7.14–7.33 (m, 10H), 7.35–7.41 (m, 1H), 7.41–7.47 (m, 1H), 7.70 (t, J = 8.6 Hz, 2H), 8.20 (br s, 1H), 8.30 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 21.20, 39.44, 40.88, 42.45, 42.79, 103.32, 103.79, 109.15, 110.54, 111.81, 112.13, 118.34, 118.53, 120.41, 120.71, 121.80, 122.52, 122.55, 122.89, 123.05, 124.02, 124.97, 125.05, 126.56, 126.59, 129.29, 129.34, 132.94, 133.07, 134.12, 134.12, 136.18, 136.21, 138.28, 138.32 (a pair of carbons are accidentally isochronous). MS (ESI): m/z 385 $[M+H]^+$.
*(E)-3,3-Bis(1H-3-indolyl)-1-(p-tolyl)propene (**15b**).* Red-brownish solid, mp 127–128 °C (diethyl ether/petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.30 (s, 3H), 5.38 (dd, J = 7.1, 1.2 Hz, 1H), 6.50 (d, J = 15.7 Hz, 1H), 6.74 (dd, J = 15.8, 7.0 Hz, 1H), 6.91 (dd, J = 2.5, 0.9 Hz, 2H), 6.96–7.13 (m, 4H), 7.13–7.22 (ddd, J = 8.2, 7.0, 1.2 Hz, 2H), 7.23–7.31 (m, 2H), 7.35 (dt, J = 8.1, 0.9 Hz, 2H), 7.59 (dd, J = 7.8, 1.1 Hz, 2H), 7.92 (br s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 21.15, 37.42, 111.05, 118.51, 119.21, 120.00, 121.87, 122.53, 126.20, 126.95, 129.10, 129.77, 131.29, 134.87, 136.62, 136.70. MS (ESI): m/z 363 $[M+H]^+$.
*3-[4-(Methylsulfonyl)-2-nitro-1-(p-tolyl)but-2-en-1-yl)-1H-indole (**16b**):* isolated as a brown-solid ca. 4:1 *Z*:*E* mixture after crystallization from toluene/petroleum ether: only the NMR signals for the main (*Z*)-isomer are completely described. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.35 (s, 3H), 2.85 (s, 3H), 3.98 (dd, J = 14.7, 7.8 Hz, 1H), 4.12 (dd, J = 14.7, 8.4 Hz, 1H), 5.73 (td, J = 8.3, 1.3 Hz, 1H), 5.82 (s, 1H), 6.72 (dd, J = 2.5, 0.9 Hz, 1H), 7.08–7.29 (m, 6H), 7.34–7.46 (m, 1H), 7.49 (d, J = 7.3 Hz, 1H), 8.13 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 21.1, 40.7, 45.4, 53.7, 111.7, 113.9, 118.1, 118.6, 120.1, 122.8, 124.6, 125.7, 128.2, 129.7, 134.4, 136.7, 137.7, 159.2.MS (ESI): m/z 385 $[M+H]^+$. For the minor (*E*)-isomer, only a few signals in the ^{1}H NMR spectrum can be clearly identified: δ (ppm) 2.24 (s, 3H), 2.36 (s, 3H), 3.42–3.60 (m, 2H), 6.16 (s, 1H), 6.75 (dd, J = 2.5, 1.1, 1H), 8.20 (s, 1H); the multiplet (td) for the vinylic proton is covered by the aromatic signals, well above 7 ppm, clearly indicating its *cis* relationship with the adjacent nitrogroup.[28]
*Bis(1H-3-indolyl)(p-tolyl)methane (**17b**).* Pink solid, mp 88.0–90.0 °C (toluene/petroleum ether); lit.[29a] mp 87.0–87.3 °C (benzene). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.32 (s, 3H), 5.85 (s, 1H), 6.67 (s, 2H), 7.00 (t, J = 7.5 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 7.16 (t, J = 7.6 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 7.91 (br s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 21.09, 39.72, 110.98, 119.15, 119.85, 119.93, 121.84, 123.53, 127.04, 128.53, 128.89, 135.47, 136.63, 140.92.
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32. *Typical procedure for the reaction of dinitrobutadienes **3** with indole.* To a stirred suspension of **3** (0.5 mmol) in ethanol (8 mL) at 40 °C, indole (1.1 mmol) and zinc acetate (0.5 mmol) were added. The mixture was stirred at 40 °C for 24 h to ensure completion of reaction and then poured into water and extracted with dichloromethane; the organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by column chromatography using hexane/ethyl acetate (10:1) to give **19**, **20** and **25**.
*3-Nitro-1,4-bis(p-tolyl)-9H-carbazole (**19b**).* Yellow solid, mp 213–214 °C (dichloromethane/petroleum ether). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.49 (s, 3H), 2.53 (s, 3H), 6.74 (d, J = 8.0 Hz, 1H), 6.97 (t, J = 5.1 Hz, 1H), 7.48–7.29 (m, 8H), 7.62 (d, J = 8.0 Hz, 2H), 8.16 (s, 1H), 8.60 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 21.59, 21.81, 111.20, 120.78, 122.16, 123.11, 123.23, 123.97, 124.34, 127.16, 128.36, 128.48, 129.89, 130.57, 132.44, 133.64, 133.96, 138.13, 138.85, 139.43, 140.52, 142.22. EI (relative intensity): m/z 392(100) [$M^{+\bullet}$], 375(9), 362(13), 347(14), 331(34), 316(9), 254(12), 171(19), 164(48), 158(48), 151(22), 145(13), 139(13), 119(9), 91(5). UV–vis ($CHCl_3$) λ_{max} 230, 281, 306, 344 nm.
*2-Nitro-1,4-bis(p-tolyl)-9H-carbazole (**20b**).* Yellow solid, mp 124–125 °C (dichloromethane/petroleum ether). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.49 (s, 3H), 2.52 (s, 3H), 7.05 (t, J = 7.5 Hz, 1H), 7.47–7.32 (m, 8H), 7.65–7.53 (m, 3H), 7.77 (s, 1H), 8.19 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 21.57, 111.07, 117.14, 119.17, 120.17, 122.34, 123.47, 124.02, 127.59, 128.77, 129.07, 129.57, 130.28, 130.99, 136.29, 137.11, 138.39, 138.65, 138.83, 141.39, 145.36 (a pair of carbons are accidentally isochronous). EI (relative intensity): m/z 392(100) [$M^{+\bullet}$], 375(6), 362(14), 347(17), 331(23), 316(7), 254(12), 171(10), 164(52), 158(46), 151(25), 145 (15), 139(13), 119(8), 91(5). UV–vis ($CHCl_3$) λ_{max} 242, 260, 346 nm.
*2,3-Dinitro-1,4-bis(p-tolyl)-9H-carbazole (**25b**).* Yellow solid, mp 267–268 °C (dichloromethane/petroleum ether). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 2.49 (s, 3H), 2.52 (s, 3H), 6.90 (d, J = 8.3 Hz, 1H), 7.09–7.00 (m, 1H), 7.41–7.48 (m, 10H), 8.40 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 21.61, 21.71, 111.50, 118.88, 121.43, 122.82, 123.30, 128.07, 128.38, 128.74, 128.82, 129.96, 130.37, 130.64, 131.25, 137.74, 139.47, 140.14, 141.27 (three pairs of carbons are accidentally isochronous). EI (relative intensity): m/z 437(100) [$M^{+\bullet}$], 407(7), 374(9), 361(20), 345(20), 332(17), 316(12), 255(9), 171(16), 164(63), 158(51), 151(34), 146 (28), 138(14), 119(10), 91(12).
33. *X-ray crystallography*. Single crystals of **19b** were submitted to X-ray data collection on an Oxford-Diffraction Xcalibur Sapphire 3 diffractometer with a graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293 K. The structure was solved by direct methods implemented in SHELXS-97 program.[34] The refinement was carried out by full-matrix anisotropic least-squares on F^2 for all reflections for non-H atoms by means of the SHELXL-97 program.[35] Crystallographic data (excluding structure factors) for structure **19b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-836410. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).
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